

# *Advances in* **ORGANOMETALLIC CHEMISTRY**

EDITED BY

**F. G. A. STONE**

DEPARTMENT OF INORGANIC CHEMISTRY  
SCHOOL OF CHEMISTRY  
THE UNIVERSITY  
BRISTOL, ENGLAND

**ROBERT WEST**

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

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## List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

A. G. BROOK (95), *Department of Chemistry, University of Toronto, Toronto, Canada*

JAMES P. COLLMAN (53), *Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina*<sup>1</sup>

HENRY GILMAN (1), *Department of Chemistry, Iowa State University, Ames, Iowa*

W. P. GRIFFITH (211), *Department of Inorganic Chemistry, Imperial College, University of London, London, England*

K. KÜHLEIN (241), *Institute of Organic Chemistry, Justus Liebig University, Giessen, Germany*<sup>2</sup>

J. J. MROWCA (157), *Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware*

W. P. NEUMANN (241), *Institute of Organic Chemistry, Justus Liebig University, Giessen, Germany*

G. W. PARSHALL (157), *Central Research Department E. I. du Pont de Nemours and Company, Wilmington, Delaware*

WARREN R. ROPER (53), *Department of Chemistry, University of Auckland, Auckland, New Zealand*

<sup>1</sup> *Present address:* Department of Chemistry, Stanford University, Palo Alto, California

<sup>2</sup> *Present address:* Farbwerke Hoechst A. G., Frankfurt/Main, Germany

# Some Personal Notes on More Than One-Half Century of Organometallic Chemistry

HENRY GILMAN

*Department of Chemistry  
Iowa State University  
Ames, Iowa*

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It was in 1912 that I carried out my first organometallic reaction. This was done as part of laboratory work in an elementary course in organic chemistry. The reaction was between acetone and methylmagnesium

iodide to give *tert*-butyl alcohol. This experiment was a bit of a disappointment, even though some of the *tert*-butyl alcohol was obtained. From the lectures we had learned how versatile was the Grignard reagent for obtaining the widest variety of compounds; and there was an extra bit of pleasure and a challenge in writing out "paper syntheses" on some assigned work and in examinations. Perhaps very few less satisfactory syntheses could have been selected for beginners in laboratory work because of the low yield of product obtained. I vowed that if I ever taught beginners, I would select a Grignard reaction which gave good yields of a solid which could be conveniently isolated; and this was done several years later, as part of a beginning laboratory course I taught, with a reaction between ethyl benzoate and phenylmagnesium bromide to give triphenylcarbinol.

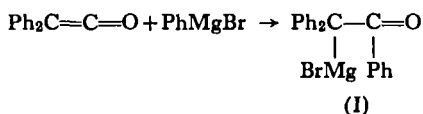
My subsequent academic training through my Ph.D. work did not include any laboratory experiments involving organometallic chemistry. For a one-year period after my bachelor's degree, I went to Europe; and of this time spent more than one-half year with Professor Staudinger in Zürich, where I did a little work on diazo compounds. At that time Staudinger was interested in both azo compounds and in ketenes. It was not surprising, therefore, that he mentioned in a general discussion the possibility of preparing diazoketene,  $\text{N}\equiv\text{N}=\text{C}=\text{C}=\text{O}$ . I observed that this might be a rather unstable compound, having four units of unsaturation in a compound containing only five atoms. He agreed, but suggested we visit a room in the basement of the Chemistry building at the ETH (Eidgenössische Technische Hochschule) which had one rather small incandescent red bulb to reduce risks that might be involved in photochemical activation. Shortly thereafter, I completed the work on which I was engaged and the time had come for me to move on to Oxford with Professor W. H. Perkin. Therefore, I did not make use of that unusual laboratory and I do not know what was subsequently done with the exciting diazoketene problem.

On returning to Harvard, I completed my graduate work with Professor E. P. Kohler, who was not only an excellent and polished lecturer, but also a superb laboratory worker. While at Bryn Mawr College and later at Cambridge, he did classic work which laid a firm foundation for the understanding of conjugated systems, and particularly for 1,4-additions of Grignard reagents to  $\alpha,\beta$ -unsaturated carbonyl systems.

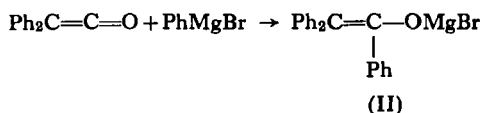
After some war work, instructing at Cambridge, and then at the University of Illinois (where Roger Adams had gone a few years earlier, and with whom I had done some research work as a senior), I went on to Iowa

State at Ames (2a). Here I did my first research work on organometallic chemistry. The problem was one involving the mode of addition of phenylmagnesium bromide to diphenylketene. The idea for it came from some regular class lectures given by Kohler. I had not done research prior to that time either with the Grignard reagent or with ketenes.

Two possible modes of addition could be involved primarily in this reaction. First, there might be addition to the olefinic linkage.



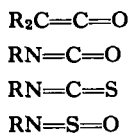
Second, there might be addition to the carbonyl group.



The product isolated, triphenylvinyl alcohol (or its ketone), would be expected to result by either mode of addition. In a sense, these involved a sort of "impossible" reaction because ketene additions were then interpreted as additions to the olefinic linkage, and at that time there was no known addition of the Grignard reagent to an olefinic linkage. One way of throwing light on the course of the reaction was to treat the intermediate compound with benzoyl chloride to see whether the —MgBr was on carbon or oxygen. The product isolated was the benzoate of triphenylvinyl alcohol. This supported structure (II) and established the general hypothesis that additions to ketenes involved initially the carbonyl group rather than the olefinic linkage.

This work, with Heckert, was our first publication in the area of organometallic chemistry (24). It was not only a pleasant beginning, but gave as much satisfaction as any subsequent work.

The finding that the Grignard reagent did not add to diphenylketene in a manner like that generally accepted then for addition reactions to ketenes, led logically to a study of some other related terminal cumulated unsaturated systems:



The results with all of these types proved or indicated that phenylmagnesium bromide added initially to the terminal unsaturated linkage. It was in connection with these studies that we observed a highly unusual transformation.

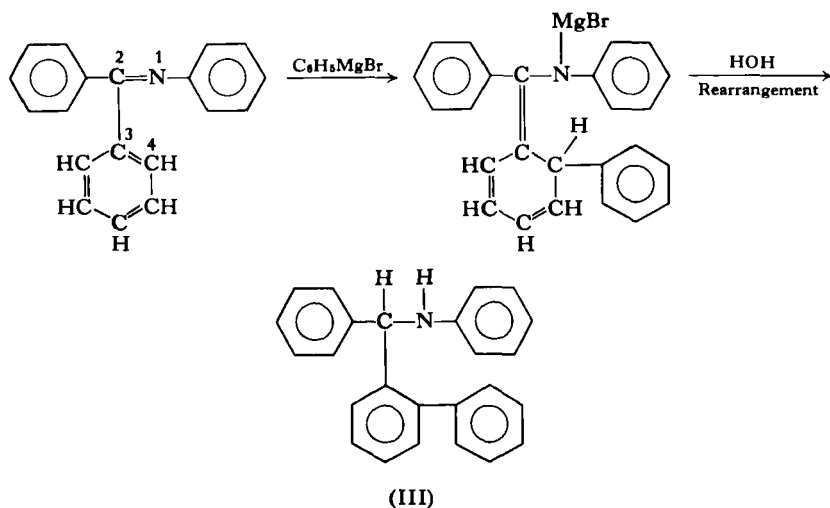
In the reaction of each of these terminal cumulated unsaturated systems with phenylmagnesium bromide in ether, the reaction stops at the terminal unsaturated group even with a liberal excess of phenylmagnesium bromide and extended refluxing in ether. This was hardly unexpected with ketenes inasmuch as subsequent addition to an ethylenic linkage was unlikely on the basis of information then available on the nonaddition of  $\text{RMgX}$  to isolated olefinic linkages. The situation, however, was different with types like phenyl isocyanate and phenyl isothiocyanate, because it was known that organomagnesium halides add to the  $\text{—N=C—}$  group. Accordingly, it was expected that when phenyl isocyanate (or phenyl isothiocyanate) was refluxed for an extended time and at elevated temperatures with an excess of  $\text{PhMgBr}$ , a second molecule of the Grignard reagent should add to the  $\text{—N=C—}$  linkage. The chief product isolated contained neither oxygen nor sulfur and was shown to be *N*-(*o*-phenylbenzhydryl)aniline (III). Incidental to an examination of the course of the reaction it was postulated that benzophenone-anil,  $\text{Ph}_2\text{C=NPh}$ , was an intermediate, and it was then established that this anil as well as  $\text{PhN=C=O}$  and  $\text{PhN=C=S}$  gave (III) under forcing conditions. What apparently happens in these cases is an "unlocking of the benzene ring" or the highly unusual type of 1,4-addition to a conjugated system that is part aliphatic and part aromatic; the following transformations were depicted to account for the formation of (III): No reaction of this kind had been described at that time. Shortly thereafter this type of reaction was found to be rather general, particularly as the result of the splendid studies by E. P. Kohler, and by Fuson [who wrote an excellent review article on it (12)].

## I

### GRIGNARD REAGENTS: SOME GENERAL PROCEDURES AND TECHNIQUES

Quite early in our studies we became aware of the desirability and the necessity of developing new and improved laboratory procedures for operations involving Grignard reagents. Methods for quantitative analysis were paramount, and in this as well as many other studies we were fortunate

in having a background of prior studies by others. Within the obvious limitations of a personal account of this kind, it is out of the question to make appropriately adequate references to the work of others, just as it is not possible to include adequate mention and references to our own work.



This presentation carries with it an inordinately high degree of selectivity. Actually, because of our numerous publications we have been compelled, to our deep regret, to make some almost random selections and thereby to commit gross omissions of some equally worthy and interesting work. To offset this in part we have included in a series of general references (1, 2, 4, 9-11, 13-23, 26-35, 37, 43-46) citations to review articles, chapters, etc., on some aspects of part of our work which contain, in turn, appropriate references to pertinent work by others.

In the several procedures examined for the quantitative determination of RMgX compounds, the one which we found most convenient was the simple acid-titration method. In their classic book on the Grignard reagent, Kharasch and Reinmuth (36) evaluate the several procedures and conclude: "Organic chemists appear to have accepted the acidimetric method rather generally, possibly because of the extreme simplicity of its technique and the consistency of its results. Incidentally, smaller aliquot portions of Grignard solution and lower concentrations of standard acid and base than those originally proposed by Gilman *et al.*, have been found entirely satisfactory."



Another important tool developed was a qualitative test, namely, the Michler's ketone Color Test I. This we found to be uncommonly helpful over the years, and we looked upon it as one of the most useful and important reactions in organometallic chemistry. As our studies extended into other areas such as those involving organolithium compounds, other color tests were developed to differentiate  $\text{RMgX}$  from  $\text{RLi}$  compounds, and also to differentiate between types of  $\text{RLi}$  compounds.

With suitable procedures for the qualitative and for the quantitative estimation of such classes of organometallic compounds, we were provided with the essential means for examining a series of significant factors. Among these were such aspects as (1) optimal conditions for the preparation of important types of organometallic compounds; (2) catalysts for the preparation of some  $\text{RM}$  compounds, otherwise preparable with difficulty; (3) effects of a wide variety of solvents; (4) stability of some  $\text{RM}$  compounds or their solutions; and (5) relative reactivities of some  $\text{RM}$  compounds.

We might mention first that it was our practice whenever exploring a new group of organometallic compounds to try to devise useful qualitative and quantitative procedures. This applied not only to the more conventional, synthetically useful types such as  $\text{RMgX}$  and  $\text{RLi}$ , but also to species such as  $\text{R}_3\text{SiM}$ ,  $\text{R}_3\text{GeM}$ ,  $\text{R}_3\text{SnM}$ , and  $\text{R}_3\text{PbM}$ .

The determination of optimal conditions for the preparation of some moderately reactive organometallic types provided certain unexpected dividends, described elsewhere, such as the benzhydryl radical ( $\text{Ph}_2\text{CH}\cdot$ ) formed incidental to the preparation of  $\text{Ph}_2\text{CHMgX}$  (then an inaccessible type). Also, the development of satisfactory conditions for the synthesis of allylmagnesium halide types (prior to which time they were unavailable and used indirectly by their formation *in situ* in the presence of reactants by the Barbier technique) was of particular significance in some relative reactivity and analytical studies. In connection with the benzyl and related Grignard types, mention should be made of the extensive studies with J. E. Kirby on the rearrangement reactions of benzylmagnesium halides and their congeners.

An anecdote may be in order relative to an aspect of catalysts for the preparation of some Grignard reagents. After a series of experiments revolving around the known catalytic effects of copper and some of its compounds, we found that an alloy of magnesium with  $12\frac{3}{4}\%$  of copper was highly effective when used in a fine state and activated by iodine. The required amount of this catalyst was extremely small. At the request of a

friend, we had made up about 100 gm of the material, and the price charged to him was merely for the grinding by the shopman of the bar of magnesium-copper alloy (which was given us without charge). Our friend, who wished to make it available to organic chemists by purchase as a service to the profession, asked if we would have any objections to his increasing the sale price. This he wished to do to discourage eager indiscriminating purchasing agents from buying much more than could actually be used over a long period of time, and not because he sought to make a profit on an inexpensive item of which extremely small amounts would be used only occasionally.

A considerable amount of work was done in the early stage of our studies on the Grignard reagents, using both simple and mixed solvents. It is interesting to recall that one of the first studies involved the best way of preparing anhydrous ether, using a variety of desiccating agents, at a time when anhydrous ether was relatively inaccessible and rather costly. One of these solvent studies culminated with the extreme case of using no added solvent at all in the high-yield preparation of phenylmagnesium chloride from chlorobenzene and magnesium.

Apropos extremes in the stability of some organometallic compounds in solvents, it occurred to us that it might be of interest to examine the stability of methylmagnesium iodide in ether over an extended period, in a glass-sealed container at room temperature, and not exposed to direct light. The particular sample was opened after 20 years of standing, and there was essentially no change in titration value. The Michler's ketone Color Test I was positive, and the yields of typical derivatives were high.

## II

### ORGANOLITHIUM COMPOUNDS

In the early development of organometallic chemistry, those organometallic compounds which found widest applicability for synthetic purposes were the organozinc and organomercury compounds. The picture changed dramatically with the advent of Grignard reagents. Another phase came with the organolithium compounds, because of their complementary and special properties which serve to set them apart from other types. In our initial studies it was somewhat of a chore, even with the very small-sized experiments carried out, to prepare the metal in a suitable form for reaction. What was available then was lumps of the metal. In turn these were chiseled,

cut, flattened, converted to shot, and to dispersions, before we learned what form was most suitable for laboratory use. One of the common techniques was to flatten portions of the bulk metal into ribbon and then with scissors to cut very small pieces which fell into the flask through an emerging stream of dry nitrogen. This was less tedious than our former procedure of using a rasp file to admit filings by a like mode of addition. From this we soon learned the better forms of the metal to use for laboratory experiments. As our uses for organolithium compounds expanded in studies on relative reactivities, exchanges, etc., we established optimal conditions for the preparation of the requisite compounds. These were special and varied depending on the nature of the RLi compound and the reactions to be carried out with them. Prior to our work on organolithium compounds, studies had been carried out by W. Schlenk, C. S. Marvel, G. Wittig, and, of particular noteworthiness, by K. Ziegler, who used not only ether but also benzene and cyclohexane as reaction media.

Three items of interest might be mentioned as they relate to solvents and RLi compounds. One involved our initial and significant use of petroleum ether for the reaction medium in organolithium preparations. A second item concerned the observation that methyllithium might be a reagent of choice in some Zerewitinoff reactions because of its stability in ether, and because of the greater solubility of units such as  $\text{—OLi}$  over the corresponding  $\text{—OMgX}$  compounds formed in reactions leading to the evolution of methane. Third, were some formulations of special conditions for preparing and using RLi compounds in tetrahydrofuran, which is often a solvent of choice because of the enhanced reactivity with some substrates in this medium.

Related to solvents for RLi compounds such as tetrahydrofuran is the keeping quality of RLi solutions in THF. Unlike the relative stability of RMgX in THF (which solvent H. Normant has used so effectively) many of the RLi compounds must be handled with particular care in THF to avoid extensive decomposition at moderate temperatures. We later showed that this decomposition or cleavage of THF by reagents such as triphenylsilyllithium was a procedure of choice for the synthesis of compounds such as  $\delta$ -triphenylsilylbutanol by ring cleavage of the THF.

At the beginning a comprehensive study was made of solvents, particularly ether. When some theoretical consideration suggested the probable advantages of *sec*-butyllithium and of *tert*-butyllithium for reactions such as metalation, we established that such RLi compounds could be made

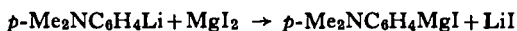
conveniently and in high yields in petroleum ether. There were, of course, other experimentally established advantages in the use of petroleum ether for the preparation of RLi compounds, and among them were their high stability and storage properties in this solvent, particularly in comparison with a wide series of solvents such as ethers. These studies helped significantly to extend the usefulness of RLi compounds such as *n*-butyllithium. This applies not only to laboratory experimental quantities but also to massive bulk industrial amounts. For example, in 1961 the Foote Mineral Company was the first to ship by tank truck about 3800 lb of active *n*-butyllithium, 15% by weight in hexane solution. Then in 1967 they shipped a railroad tank car carrying about 5000 lb of active *n*-butyllithium, also 15% in hexane. Incidentally these instances illustrate dramatically the growing importance of organolithium chemistry, for not many years ago we struggled to conduct laboratory preparations on about a 0.1 mole scale. It should be remarked that apparently the most widely used RLi compound is *n*-butyllithium, but others have grown greatly in interest because of their availability to laboratory workers. Incidentally it should also be noted that some highly extensive industrial applications by others of Grignard reagents (such as the preparation of organolead compounds) involve "captive" uses of intracompany-produced reagents in particular industrial applications.

It is relevant for comparative purposes to recall here a statement we made (14) more than 30 years ago on an aspect of the industrial uses of organometallic compounds: "It is doubtful that any other group of organic compounds combines at the same time an astonishingly high utility in the laboratory with an equally low usefulness in the works."

In our comparative reactivity studies it was necessary to go beyond establishing optimal conditions for the formation of RLi compounds in a given medium, and beyond examining a variety of solvents, as well as determining the stability of the reagents under varying conditions. Here it was helpful to supplement the useful Michler's ketone Color Test I with other qualitative analytical tools. Several additional color tests were developed, some of them as by-products of studies on metalation and halogen-metal exchanges. These additional color tests have been useful for several purposes, such as differentiating RMgX compounds from RLi compounds, and also some organolithium compounds from other organolithium compounds as well as from some other RM compounds besides the Grignard reagents.

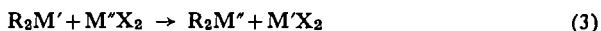
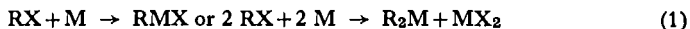
Also, analytical procedures were developed for the quantitative analysis of organolithium compounds. Fortunately these had the merit for our studies in being convenient, rapid, and not requiring any special apparatus or equipment beyond conventional laboratory glassware.

Organolithium compounds admirably supplement the Grignard reagents, and are not only more reactive than the RMgX compounds but can be prepared and stored in solvents which generally are more convenient than ether. However, when ether is used, for example with methyllithium, there are properties which we have found to recommend them above the corresponding MeMgX compounds. The variety of methods which can be used for the preparation of organolithium compounds exceeds appreciably procedures for the synthesis of Grignard reagents. Some of these are mentioned later in the sections on metalation, halogen-metal exchange, and metal-metal exchange. The interconvertibility of organometallic compounds in which an RLi compound is used can be illustrated by a selected reaction related to studies with J. Swiss and others and useful in one of the color tests.



The prompt conversion of organolithium compounds to the corresponding Grignard reagents by means of magnesium bromide or iodide is of preparative value for the synthesis of some RMgX compounds otherwise obtained with difficulty. For example, *p*-dimethylaminophenylmagnesium bromide is prepared in ether from the halide with difficulty and in poor yields, whereas *p*-dimethylaminophenyllithium is obtainable in 96% yield. The latter compound is readily converted to the corresponding RMgX compound by magnesium iodide, as illustrated above. At that time it was observed that the reaction might also prove of value in converting some readily accessible mono- and organopolysodium and organopolypotassium compounds to the corresponding RLi and RMgX types.

This raises a general consideration of the preparation of RM compounds. There are many hundreds of publications on the preparation of organometallic compounds. As an evidence of changes which have taken place since the writing of our chapter in the treatise (14), we there discussed a rule-of-thumb generalization on the preparation of many RM compounds by appropriate reactions from a selected organometallic compound, such as the Grignard reagent. It would seem desirable to mention three syntheses of wide application.



Basically, therefore organometallic compounds derive from interaction of an RX compound with a metal or its alloy or amalgam. This applies particularly to the preparation of organozinc, -magnesium, and -lithium compounds, which are among the most effective types for the transformations illustrated in reactions (2) and (3). The historically important organozinc compounds have been largely superseded for synthetic purposes by the magnesium and lithium compounds which are less inflammable, less toxic, and more conveniently manipulated. Although organozinc and -mercury compounds still find use for the synthesis of other organometallic compounds, it is significant that many zinc and mercury compounds now are best prepared from the corresponding organomagnesium and -lithium compounds. In general, a more reactive organometallic compound is formed from a less reactive compound in (2); and a less reactive organometallic compound is formed from a more reactive compound in (3). These generalizations apply to all organometallic compounds so that one may expect to use any RM compound for the synthesis of all other organometallic compounds. Something approaching this has been realized with the Grignard reagent, which has been used at one time or another for the preparation of practically all other organometallic compounds: the more reactive being prepared from RMgX and a metal, and the less reactive from RMgX and a metallic halide. These useful, broad generalizations are as applicable to RLi as to RMgX compounds. However, today expanding studies in this area are uncovering new and special synthetic procedures. Some of these are with organoaluminum, organosodium, and organoboron compounds, the last type in extensive current studies by H. C. Brown. Also, we have shown that a number of the exchange reactions, as mentioned elsewhere, are reversible. For example, a more reactive RM compound can be made from an RMgX or RLi compound and a metallic halide.

### III

#### RELATIVE REACTIVITIES

Very early in our studies on the Grignard reagent we thought it would be interesting to compare organoberyllium compounds with the highly versatile Grignard reagents. As an indication of what has happened over

these decades, an historical note should be mentioned. At that time there apparently was no beryllium metal of quality available in this country. One to whom we wrote on this subject was Dr. Charles L. Parsons who, while teaching in New Hampshire, had written a monograph (39) on the chemistry of beryllium. He later became secretary of the American Chemical Society, a position he filled with effectiveness and vigor for many years. I wrote him to inquire whether he had any of the metal, or where I might turn to purchase a small amount for experimental purposes. He replied on November 29, 1921, and the following are extracts from that letter:

"I regret to say that I have no metallic beryllium, nor have I ever seen any which I have felt was pure. I do not believe that there is a gram of pure metallic beryllium in the world today. I am prepared to state that I would not take a contract to furnish you with a gram of pure metallic beryllium for \$10,000, and I have no idea where it can be obtained. I do not wish you to get the idea, for a moment, that I mean to indicate that pure metallic beryllium cannot be made, for such is farthest from my thoughts. I simply worked two years trying to get it myself before I left New Hampshire, and finally came to the conclusion that my own time was too valuable to work on the subject further. The difficulties are unquestionably great."

About two years later, I did obtain a somewhat impure small sample from Professor Simonis, and about 0.1 gm from Professor Stock, which he shared with me from the very small piece he had. It is interesting to reflect that pure metallic beryllium became quite available only a few years later at something appreciably less than \$10,000 a gram. From beryllium metal and from beryllium chloride we prepared the  $RBeX$  and  $R_2Be$  types, and obtained evidence to indicate that the following equilibrium is quite probable under certain conditions:



and is of the kind shown by Schlenk with the analogous Grignard reagents. By way of comparison with the Grignard reagents, we reported that dimethylmagnesium was distillable from methylmagnesium chloride under reduced pressure to give the dimethylmagnesium complex free of halogen.



This apparently was the first reported case of a volatile organomagnesium compound. It is possible to ether-distill dimethylberyllium free of

halogen, but a like operation may or may not take place with alkylmagnesium halides where both the  $R_2Mg$  and the  $MgX_2$  are ether-distillable. Some dialkylmagnesium compounds ( $Me_2Mg$ ,  $Et_2Mg$ , and  $n\text{-}Bu_2Mg$ ) can be sublimed under reduced pressure.

The number of comparisons among different types of organometallic compounds continued to accrue. Concurrently we had examined the relative reactivities of different members of a given series, as was the case with the broad class of organomagnesium compounds. This interest in comparing the relative reactivities of organometallic compounds was systematically developed as new types became available. A highly useful tool in this connection was the Entemann-Johnson series of relative reactivities of some functional groups towards a selected organomagnesium compound, such as phenylmagnesium bromide. As our studies expanded, it became evident that there were changes in the order of reactivity of functional groups towards organometallic compounds other than  $RMgX$ .

It is interesting to recall that a particular stimulus for an intensification of our studies on the relative reactivities of organometallic compounds came from a special source. When outlining the proposed contents of the chapter on "Organometallic Chemistry" for the advanced treatise in organic chemistry (14) which we edited, we felt the need of some pattern into which we might weave the relatively disparate threads that comprised organometallic chemistry. The thought occurred to us that relative reactivities of the different types might help to bring more order and improved organization to the subject matter. With this in mind, new types of organometallic compounds were developed and studied; and collaterally comparisons were made of relative reactivities.

The chapter also brought with it a highly unexpected dividend. In the first edition of the book we mentioned that the relatively few investigations of the organometallic compounds of gallium and indium were due to the comparative inaccessibility of these metals. One of my graduate students took the textbook home for some possible collateral reading during the Christmas holidays. The book was left on the family reading table where her father found it and turned to sections of interest to him. As he was a scientist associated with a large zinc smelting company in the east, he read with interest what I had written about the relative inaccessibility and high cost of gallium and indium. He remarked to her that over a period of time they had accumulated small experimental working quantities of the metals, and that he would be pleased to send them to me. This he did.



Over a period of years we prepared and examined an uncommonly broad array of organometallic compounds. Actually, studies were carried out on organometallic compounds which involved essentially all available metals and metalloids together with some of their derivatives (such as halides). While these studies were in progress, we wrote the following in our chapter (14) more than 30 years ago:

"One may predict that organometallic compounds of all the metals will be prepared. The development of organometallic chemistry has provided numerous hypotheses concerning the limits of preparation of these compounds. Gradually, the hypotheses have been narrowed down so that fewer and fewer metals are included in the groups which are said to be incapable of forming organometallic compounds. Some of these earlier hypotheses have been useful in pointing out those organometallic compounds which will be prepared with difficulty; other hypotheses have undergone revision necessitated by the preparation of organometallic compounds the existence of which had been denied."

From our extensive studies there evolved a series of empirical rules or generalizations on relative reactivities. These were very helpful in several respects. For one thing they added a fillip of excitement to the correlation of otherwise unrelated phenomena associated with the highly diverse properties of organometallic and organometalloidal compounds. This made it possible after a while to predict some essential properties and chemical behavior with moderate success. In short we felt after some series of studies (such as those on the relative reactivities of organolithium, -sodium, -potassium, -rubidium, and -cesium compounds) that a semblance of useful order was being created. Concurrently new types of compounds were prepared, and with them some novel reactions and techniques; always, where possible, information on such aspects as structure, stability, and analytical procedures was sought. In order to put these observations in better perspective, it may be appropriate to refer to some of our remarks on another occasion: (19)

"Speaking of newer techniques, many of which were not available only a few decades ago, it is interesting to project and predict further advances in our knowledge of the structure of some organometallic compounds. For example, the structure of the Grignard reagent has for 65 years been sporadically explored, culminating in recent years in a great outburst of activity. It is probable that in the next 65 years newer concepts and

techniques of a kind not now on the horizon will continue to keep alive spirited research on the structure of just this one of many types of organometallic compounds. Fortunately, as has been remarked on other occasions, it is gratifying that the ultimate refinement and precision appear unattainable."

The rules of reactivity of organometallic compounds were very helpful. For example, 10 years ago Rochow, Hurd, and Lewis made the following observations in discussing the organization of the subject matter in their book on the chemistry of organometallic compounds (40). "Considerable use has been made of the classical studies of Gilman in this field, including his valuable reactivity series, and we are grateful for the guidance thus offered." Then after discussing the several rules, they remarked: "In fact, all ten of Gilman's rules of reactivity and replacement are in accord with the principle of bond polarity and offer extensive corroboration of these principles." These somewhat roseate hues have dimmed with the passage of time and the accumulation of new information. Practically all of our empirically determined reactivity rules were established principally from a series of studies carried out in ether. We now know the pronounced effect of solvents on reactivities. These and some related observations are made in the most recent book which has just appeared, by Eisch, on "The Chemistry of Organometallic Compounds" (8).

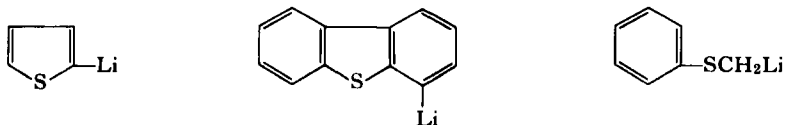
Our rules of reactivity were determined by various reactions. The functional groups used in evaluation in some studies were the carbonyl group, the nitrile group, and the double bond of some unsymmetrically substituted olefins.

#### IV

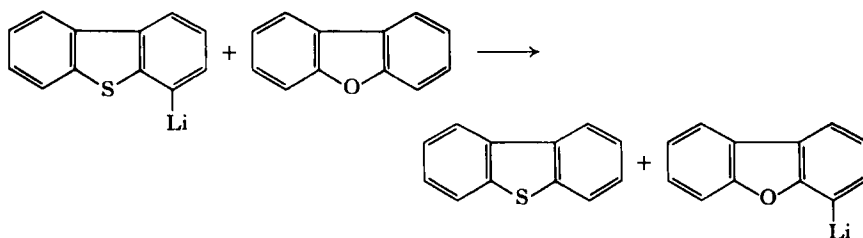
#### METALATION

The term metalation was originally proposed by us about 35 years ago to denote the replacement of hydrogen bonded to carbon by metal to yield a true organometallic compound. We early observed in connection with studies of dibenzofuran types that metalation tended to yield ortho products. This direction to the ortho position, usually unmixed with para or other isomers, distinguishes the metalation reaction from the more familiar types of substitution, and makes possible the preparation of many compounds not readily available through other routes. This tendency to replace a nuclear

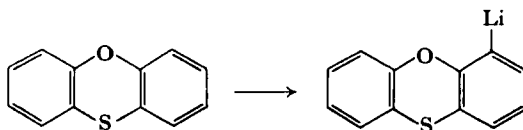
hydrogen atom ortho to the hetero atom, or a lateral hydrogen atom on a carbon adjacent to the hetero atom, is illustrated by the metalation (using *n*-butyllithium) of thiophene in the 2-position; dibenzothiophene in the 4-position; and methyl phenyl sulfide on the methyl carbon atom to give the following organolithium compounds:



Other observations soon followed to help formulate rules for the prediction of the position of metalation. One of these is that the ether linkage has a greater activating effect in metalation than the sulfide linkage. Among experiments carried out to establish this principle are the three following representative reactions: (1) When a mixture of dibenzofuran and dibenzothiophene reacts with an insufficient quantity of *n*-butyllithium, only the dibenzofuran is metalated. (2) 4-Dibenzothiényllithium metalates dibenzofuran in the 4-position, but the reverse reaction does not proceed.



(3) The metalation of phenoxathiin by *n*-butyllithium occurs ortho to the oxygen rather than to the sulfur atom.



In an expected fashion an extensive series of investigations concerned with mechanisms of reaction, optimal conditions involving different kinds of organometallic compounds, variations in solvents, etc., revealed the invalidity of any rigid generalizations. Among these was the meta metalation

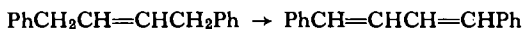
of compounds such as triphenylamine, triphenylphosphine, and triphenylarsine; and a so-called anomalous orientation effect by some organometallic compounds such as phenylcalcium iodide. Of interest is the metalation of dibenzothiophene in the 4-position by diethylstrontium, whereas metalation by the somewhat related phenylcalcium iodide takes place in the 3-position. It is pertinent to remark in this connection on our study of the effect of temperature, and of the type of RLi compound used, on the yield of product from the metalation of the sensitive benzothiazole. This reaction is peculiar among metalations in its high speed and in the fact that a low temperature must be maintained to prevent decomposition of the product. It was found that methyllithium, phenyllithium, and *n*-butyllithium all effect metalation in yields exceeding 68%; the best yield (90%) was obtained with *n*-butyllithium at  $-75^{\circ}\text{C}$  by interrupting the reaction immediately after all the RLi had been added. At the time, this study appeared to be the only one in which careful attempts were made to find optimal conditions for the metalation of a specific compound needed in another research. They indicate that whenever a high yield is of critical importance, an investigation of the influence of solvent, temperature, and metalating agent may be worthwhile. In routine metalations, however, considerations of convenience and economy will generally dictate the use of *n*-butyllithium in boiling ethyl ether. It is interesting to reflect on the changes in recent years where the need may be to use forcing conditions in metalations, and where these have been so dramatically augmented by the use of complexing agents such as TMEDA (tetramethylethylenediamine). The most significant feature in all of this is the possibility of markedly improving yields by varying experimental conditions by an admitted Edisonian approach.

It is also possible to effect polymetalation by selective reactions over a rather broad range. Whereas, RLi compounds generally monometalate types such as dibenzofuran, the more reactive organometallic compounds such as RK, RRb, and RCs give dimetalation. There appears to be a reasonably satisfactory correlation with metalation and relative reactivity of organometallic compounds. Tetra- and pentametalation of toluene by ethyllithium has been described by T. E. Talalaeva and K. P. Kocheskov. A more recent illustration of polymetalation is that by R. West on the tetralithiation of propyne to give tetralithiopropyne.

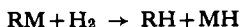
Growing out of the metalation studies were observations leading to additional color tests for organometallic compounds. These involved the metalation of benzylamine and of dibenzylamine to give bright red colors

indicative of active organometallic compounds; and also the metalation of triphenylmethane for a related purpose.

In connection with rapid metalations under unusually mild conditions, it is appropriate to mention a very rapid reaction. We attempted to metalate 1,4-dihydrodibenzofuran in ether solution by means of phenyllithium, and isolated dibenzofuran as the chief compound instead of the expected metalation product. The dehydrogenation of 1,4-dihydrodibenzofuran was also effected by *n*-butyllithium and by *n*-butylsodium. It was then shown that the related 1,4-dihydrodibenzothiophene is dehydrogenated to dibenzothiophene by organolithium and organopotassium compounds. The intermediate metalation compound was characterized, as in the case of the dehydrogenation of 1,4-dihydronaphthalene. This dehydrogenation is not restricted to cyclic compounds, for *n*-butyllithium dehydrogenates 1,4-diphenyl-2-butene to give 1,4-diphenyl-1,3-butadiene.



The above smooth ready dehydrogenation by organometallic compounds suggested that the more reactive compounds might undergo easy hydrogenolysis. This was found to be the case. Actually, some of the organoalkali compounds are cleaved by hydrogen under extremely mild conditions: room temperature, atmospheric pressure, and in the absence of any added catalyst.



We found that the order of increasing ease of hydrogenolysis of some very reactive phenylmetallic compounds is Ca, Li, Na, K, Rb, Cs. This order, together with those established for less reactive organometallic compounds by Y. Ipatieff and by H. Adkins, followed closely the order of increasing chemical reactivity of the organometallic compounds as established in other reactions. Other orders for the relative ease of cleavage or removal of groups attached to metals have been reported when the reactant is a sulfhydryl group, a carboxylic acid, etc., particularly with a reagent such as *n*-butyllithium.

Relevant to industrial applications by others of organolithium compounds in polymerization and metalation processes it is of interest to note an aspect of the growth of organometallic chemistry. In our early studies, considerable research was done in the field of Grignard chemistry. At that time there was virtually no significant technical or commercial interest in an application of the  $\text{RMgX}$  compounds. Accordingly, most of our students

who went into industry did not have any real opportunity to use the somewhat special training acquired in their thesis work. Fortunately industry did not have narrow, specialized attitudes, and, equally fortunately, the students had a good basic training in the several branches of chemistry together with adaptability and a breadth of interest. There have been exceptions to this generalization of thesis work being relatively unrelated to subsequent industrial research; one which concerns organolithium compounds and metalation is the case of a former student who did his work in this area a few decades ago and who is now using his specialized training as a research director along lines very close to his original thesis interest. The practice has changed today because of the many and widespread industrial interests in various phases of organometallic and organometalloidal chemistry. As a result, it is the exception for a graduate student in recent years to become associated with an industrial concern which is without interest in organometallic chemistry. The situation, of course, is quite different with those who go into academic work. Here there is a greater freedom of choice in their research programs, and it is interesting to observe the reasonably larger percentage who find research interests in organometallic or closely related areas.

## V

### HALOGEN-METAL EXCHANGE

The halogen-metal exchange or interconversion reaction was independently discovered by us and by G. Wittig. In one of our initial reactions we observed that *o*-bromoanisole reacted with *n*-butyllithium to yield *o*-anisyllithium and *n*-butyl bromide.



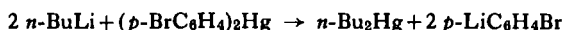
In a series of studies over an extended period we found that this reaction is of uncommon synthetic and structural importance. Although it is best effected generally by the use of *n*-butyllithium in ether, we showed that this exchange reaction proceeds with organometallic compounds of such metals as sodium, magnesium, barium, and aluminum. In an examination of different solvents, we observed that low-boiling petroleum ether appears to be especially useful for reactions involving secondary and tertiary alkyl-lithium compounds which could not be prepared readily or used conveniently in ether solution.

The reaction is of paramount importance in making available organolithium compounds which cannot be prepared otherwise or which are preparable with difficulty in low yields, where interfering side reactions occur when the metal is used directly, or, in some cases where the Grignard reagent cannot be prepared. Of particular interest is the preparation of organolithium compounds from bromides or iodides having functional groups such as hydroxyl, amino, carboxyl, azomethine, nitrilo, and sulfon-amido, which under other conditions react with the  $\text{RLi}$  compound. Among various applications, these organolithium compounds containing functional groups which can increase water solubility have found particular use in making water-soluble types for such applications as pharmacological testing.

By this reaction, numerous organolithium compounds have been prepared from heterocycles. These heterocyclic lithium compounds can be those of pyridine, quinoline, carbazole, dibenzofuran, dibenzothiophene, etc. With some of these heterocyclic systems, there are made available organolithium compounds wherein the lithium is attached to carbon atoms otherwise inaccessible. We found them to be very helpful in our extensive heterocyclic investigations.

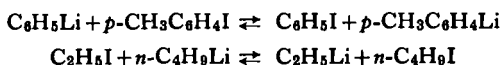
Incidentally, from these studies there was developed an additional color test to differentiate between alkyl lithium and aryllithium compounds, based on the ready exchange of bromine for lithium in *p*-bromodimethylaniline.

Generally, the metal-metal exchange is more rapid than the halogen-metal exchange. The reaction of *n*-butyllithium with di-*p*-bromophenyl-mercury, for example, yields only di-*n*-butylmercury and *p*-bromophenyl-lithium.

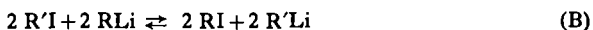
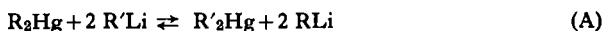


The halogen-metal exchange proceeds, as a rule, more rapidly than the hydrogen-metal exchange or metalation. Apropos the speed of some halogen-metal exchange reactions it is interesting to note that reaction of  $\alpha$ -bromonaphthalene in ether at room temperature with *n*-propyllithium gives a yield of  $\alpha$ -naphthyllithium in excess of 95% in less than  $\frac{1}{2}$  minute.

Among a series of interesting studies concerned with mechanisms, two might be mentioned here. We established that the following types of halogen-metal exchange are reversible:

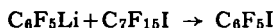


Also we observed an interesting and useful catalytic effect of organolithium compounds in some exchange reactions. This is concisely illustrated in the following reactions:



Reaction (A) is a reversible metal-metal exchange. Reaction (B) is a reversible halogen-metal exchange. Reaction (C), which is of synthetic promise, takes place with catalytic quantities of RLi compound. The mechanism of this catalyzed reaction follows from the addition of the reversible M-M reaction (A) and the reversible X-M reaction (B).

The halogen-metal exchange reaction can also be undesirable at times. One illustration, selected from a number, is the attempted coupling between pentafluorophenyllithium and perfluorinated heptyl iodide, from which there is obtained an excellent yield of pentafluoroiodobenzene, with no significant coupling.

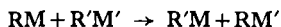


Coupling between the two reactants here can be effected by the use of catalysts.

## VI

### METAL-METAL EXCHANGE

The metal-metal interconversion reaction, as we first designated this group of reactions, was initially concerned largely with interaction of two organometallic compounds.

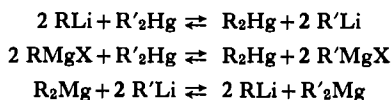


The reaction is of broad utility for the preparation of a wide variety of organometallic compounds. Attention might be directed to a review article with Jones (35) on "Methods of Preparation of Organometallic Compounds." This was published in 1954 and has the large total of 471 references. Since that time, of course, the methods of preparation have expanded greatly and part of this is due to the relatively recent high activity in the area of transition metal types.

The simple descriptive reaction given as an illustration at the beginning of this section is incomplete on two counts. First, we have shown that some



metal-metal exchanges involving the following organometallic combinations are reversible:

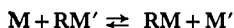


It may be pertinent to quote here from a review by Dessy (6):

"Gilman's work on these (metal-metal) exchange processes is extensive. But the position of equilibrium was determined by carbonation followed by analysis of the resulting carboxylic acids, and until recently this tended to cast some doubt on the conclusions, since shifts in equilibria could have been more rapid than carbonation. Recent NMR results by R. M. Salinger of the University of Cincinnati indicate that Gilman's general conclusion—that the groups giving the most stable carbanions prefer to be contained in the most ionic organometal—is correct. It is an interesting sign of the times to compare the cost of the two types of experiments: 10 cents' worth of Dry Ice for the former *vs* \$35,000 worth of electronics for the latter."

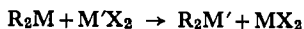
There are other equilibria, and a very wide variety of such M-M' exchanges are known. These continue to find new applications. For example, our reaction of triphenylbenzyltin and phenyllithium to give benzylolithium, has been used effectively by D. Seyferth in tin-lithium exchanges for the synthesis of types such as vinylolithium and benzylolithium.

The other count on which the simple representative reaction is incomplete lies in the descriptive term itself, that is, the following generalized reaction might also be considered to be a metal-metal exchange:



In a reaction of this type, which is historically interesting and also currently useful, one starts with but a single type of organometallic compound. Incidentally, we early observed that a rather broad generalization is that a more reactive organometallic compound is formed by the reaction of a metal with a less reactive organometallic compound, as mentioned earlier. In many of the studies involving this reaction,  $\text{R}_2\text{Hg}$  compounds have been employed as starting materials.

Another broad type of metal-metal exchange is observed in the preparation of organometallic compounds from another organometallic compound reacting with a salt.



This type of reaction has very wide applications. Another quite broad generalization with respect to this reaction is that it illustrates the general formation of a less reactive organometallic compound from a more reactive organometallic compound. In a perhaps too highly simplified generalization, it might be stated again that if one starts with the conventional Grignard reagent or organolithium compound, one can prepare from these so-called moderately reactive compounds less reactive ones by interaction with a salt.

As illustrations we might mention reaction of  $\text{RMgX}$  with  $\text{CdX}_2$ . Here, the organocadmium compound is of lesser activity. This is reflected in our initial studies of this system, which showed that the organocadmium types were less reactive than  $\text{RMgX}$  compounds toward the carbonyl group. As a consequence, reactions with acid halides and acid anhydrides were recommended as means of choice for the formation of many ketones. This has proved to be sound on the basis of its subsequent extensive uses. It is sufficient to use the reaction mixture for this purpose. Shirley (41) has reviewed the synthesis of ketones from acid halides and some  $\text{RM}$  compounds. In a paper which has just appeared (38) is the statement: "Perhaps no other method of ketone preparation has the scope of the method utilizing organocadmium reagents in their reaction with acid chlorides or mixed carboxylic-carbonic anhydrides."

Another related study involves the formation of organomanganese compounds from reaction of manganese salts with phenyllithium. Here the prediction based on generalizations of relative reactivities of organometallic compounds was confirmed by establishing the absence of 1,2-addition (and only 1,4-addition) to the conjugated system of benzalacetophenone. The reaction with benzalacetophenone was effected after washing out all lithium compounds. It has been shown with R. H. Kirby that a conjugated system such as is present in benzalacetophenone can serve to classify in a broad manner many organometallic reactions based on the type of addition. The most reactive  $\text{RM}$  compounds (such as  $\text{RK}$ ) undergo 1,2-addition; the moderately to lesser reactive types (such as  $\text{RMgX}$ ) undergo 1,4-addition; and those of intermediate reactivity show both 1,2-addition and 1,4-addition.

In connection with the participation of metals in the preparation of organometallic compounds, attention might be called to a reaction involving metallic thallium as a product. We have presented evidence for the formation of the phenylthallium radical by pyrolysis of triphenylthallium in xylene.

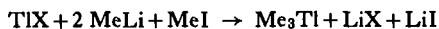
This thermally unstable "organometallic radical" is readily converted to triphenylthallium and metallic thallium, probably by way of diphenylthallium.



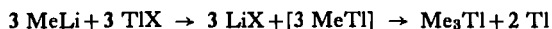
When triphenylthallium is pyrolyzed in the presence of functional groups, the resulting phenylthallium formed shows reactions of a typical moderately reactive organometallic compound. Our studies showed the decreasing reactivity of some phenyl metallic compounds to be  $\text{RMgX}$ ,  $\text{RTl}$ ,  $\text{R}_3\text{In}$ ,  $\text{R}_3\text{Ga}$ ,  $\text{R}_3\text{Tl}$ .

Another illustration of a reaction type by others which is of some industrial use is the redistribution or disproportionation reaction (3) when starting with mixed combinations of metals or metalloids.

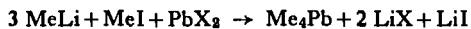
Relevant to the preparation of organothallium compounds and disproportionation it is appropriate to mention here some novel syntheses involving organothallium and some other organometallic compounds. We prepared trimethylthallium in essentially quantitative yields by three different procedures. One of these was the following:



This reaction undoubtedly involves not only the intermediate formation of thallium metal but also the direct reaction of this finely divided metal with methyl iodide. When an excess of methyllithium in ether solution was allowed to react with thallous iodide, two-thirds of the thallium was reduced to the metal and one-third appeared as trimethylthallium. Methylthallium is probably formed first, but then undergoes immediate disproportionation.



Although methyl iodide does not react with ordinary forms of metallic thallium, the very finely divided metal reacts readily with methyl iodide in ether solution at room temperature or even at  $0^\circ \text{C}$ . At that time we remarked that this type of reaction was probably not confined to thallium, and other metals such as lead and probably tin, germanium, and mercury undergo similar reactions. Shortly thereafter we found that tetramethyllead could be prepared in excellent yields by the reaction of methyllithium or methylmagnesium chloride and methyl iodide with lead halides according to the following:

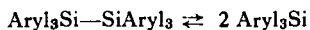


An additional feature of such transformations is the more effective use of the  $RX$  compound or the use of a lesser quantity of the  $RLi$  or  $RMgX$  compound. Incidentally, overheating of the  $Me_3Tl$  induces violent detonation. As mentioned elsewhere in connection with free alkyl radicals and with thermal stabilities, other methyl metallic compounds such as tetramethyllead, methylcopper, and dimethylcadmium decompose explosively if overheated.

## VII CATENATION

The phenomenon of catenation (*1, 21*) is observed in compounds where an element forms stable bonds to itself. It finds its fullest expression in the area of organic chemistry where many carbon atoms are united in linear, branched, and cyclic arrangements. Our studies have been largely with Group IVB types, and particularly those of silicon.

We were early interested in the possibility of dissociation of hexaaryldisilanes to triarylsilyl species.



A comprehensive study of a large variety of hexaaryldisilanes showed that there is no apparent counterpart in silicon chemistry with what has long been known in carbon chemistry, even with the incorporation of aryl groups which are known to markedly increase the dissociation of hexaarylethanes to triarylmethyls. It was incidental to our interpretation of some cleavage reactions, concerned with the ease of cleavage in some cases of the  $Si-Si$  bond, that we noted the smooth and convenient preparation of  $R_3SiM$  compounds.

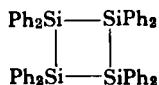


These reactions were promptly extended to not only other polysilanes having more than two contiguous silicon atoms but also to catenated compounds of other Group IVB elements.

Although we could find no satisfactory case in this area for the dissociation of disilanes to  $R_3Si$  compounds, it is interesting to note that in the splendid, pioneering studies by F. S. Kipping, he obtained a series of catenated types from the reaction of diphenyldichlorosilane with sodium to give what he designated as Compounds "A," "B," and "C." The structure he proposed for "A" was a compound having two terminal trivalent silicon atoms.



We observed that free radicals were not present and that "A" was in reality octaphenylcyclotetrasilane,



Compound "B" was shown to be the decaphenylcyclopentasilane,  $(\text{Ph}_2\text{Si})_5$ , and not the cyclic tetrasilane suggested by Kipping, nor the dodecaphenylcyclohexasilane incorrectly suggested by us initially on the basis of inadequate facilities for molecular weight determinations at that time. Compound "C" was later shown by us to be the dodecaphenylcyclohexasilane. Interestingly enough, counterparts of these compounds were later described by W. Neumann in the organogermanium and -tin series.

These catenated cyclic polysilanes, as well as others such as dodecamethylcyclohexasilane, are of special value for several reasons. We have shown that "A" and "B," in particular, can be opened by some metals, halogens, and halogen acids to give compounds of high synthetic value.

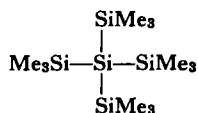


Also polysilanes exhibit unique and very interesting ultraviolet properties, some of which are mentioned later. These appear to be due to the Si—Si bond acting as a chromophore, probably through the use of vacant  $d$  orbitals of the silicon atom ( $d\pi$ — $d\pi$  double bond character). Incidentally the intense absorption maxima observed and the  $\lambda_{\text{max}}$  which increases with increasing chain length suggest applications as light-protective coatings.

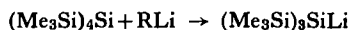
Early in our studies on organosilicon chemistry, one of the review articles (22) was concerned with relationships of analogous organic compounds of silicon and carbon, and in this we considered some reasons for the very small number of polysilanes then known (about 20). It appeared that the limited number of polysilanes might be traced, in large part, to an inadequate variety of suitable preparative procedures. We were interested in showing that there were no reasonable limits to extending catenation, and useful tools used for this purpose were the highly versatile silylmetallic types in the synthesis of a series of polysilanes containing largely phenyl groups, as well as some methyl groups. Then, in some elegant studies, M. Kumada prepared longer polysilanes containing largely methyl groups.

There is then no significant formal difference between some series of catenated carbon compounds and catenated silicon compounds.

Growing out of the catenation work was the development with C. Smith concerned with the preparation and examination of the completely symmetrical and highly branched types. One representative of this group is tetrakis(trimethylsilyl)silane.



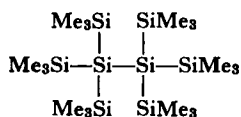
As might be expected in such types, the compounds tend to be high-melting, with high volatility, and enhanced thermal stability. A novel and very reactive type directly derivable from the parent type, is tris(trimethylsilyl)silyllithium.



With this versatile silyllithium compound, an uncommon type of conjugation is possible involving delocalization of the negative charge over the vacant *d* orbitals on the adjacent silicon atoms, i.e., *d* $\pi$ -*p* $\pi$  bonding.

Historically, it is interesting to note that a related type was prepared about 40 years ago, and its structure was recently established, with F. K. Cartledge, as tetrakis(triphenylstannyl)stannane,  $(\text{Ph}_3\text{Sn})_4\text{Sn}$ . More recently G. van der Kerk and co-workers have prepared an unusually interesting series of related types. One among them,  $(\text{Ph}_3\text{Pb})_4\text{Pb}$ , is of particular interest because it is the first catenated triplumbane type reported, and diplumbanes are generally unstable.

Another unique highly branched and symmetrical organopolysilane, developed with Harrell, has become available recently. This is hexakis(trimethylsilyl)disilane.



This compound, as might have been expected, also has a high melting point, 372°–380° C (with dec.); as contrasted with the linear isomer, octadecamethyloctasilane, which melts at 61°–62° C. Lithium and methyl lithium react with the hexakis compound to cause cleavage of the symmetrical

Si—Si bond; whereas triphenylsilyllithium and halogens effect cleavage of peripheral trimethylsilyl groups.

## VIII

### SOME FREE-RADICAL STUDIES

In a sense, organometallic chemistry may be said to have had its origin in free-radical studies. E. Frankland in 1849 was the first to isolate an organometallic compound and then establish its constitution. He set out to prepare the free ethyl radical, using zinc to remove iodine from ethyl iodide, and obtained instead diethylzinc. Then, in a series of classic investigations with inflammable and poisonous compounds, he extended his studies to some other metals. Although Frankland did not realize his primary objective of preparing alkyl radicals, it is significant that organometallic compounds provided the essential means, long years later, for the preparation of free alkyl radicals by pyrolysis. In free-radical chemistry, organometallic compounds are not only useful in themselves for the preparation of free organic radicals and the identification of free radicals, but also their use has provided a satisfactory means for establishing the existence of some elements in so-called abnormally valenced states. Frankland early in his work said that "he became impressed with the fixity in the maximum combining power or capacity of saturation in the metallic elements which had not before been suspected." The strenuously advocated case by A. Kekulé and others for a fixity in valence found support, therefore, in the early work with organometallic compounds. It is interesting to note how the whole picture of valence, as it concerned organometallic compounds, changed over the years; at first, organometallic chemistry did much to sustain the fixity of valence; later, it provided a very useful tool to establish the wide variability in valence for certain elements.

M. Gomberg, and others, in their early and epochal work establishing the existence of trivalent carbon in triarylmethyls, put to great use the synthetic possibilities of organometallic compounds for the preparation of the necessary hexaarylethanes. The organic chemist still needed experimental support for the existence of free alkyl radicals in the interpretation of many organic reactions in which there was little doubt of the intermediate participation of such alkyl radicals. It remained for F. Paneth and co-workers to demonstrate the ability of free methyl and ethyl radicals formed by pyrolysis of an organometallic compound such as tetramethyllead to set down a lead mirror in a quartz tube, and then to pick up the mirror by

free radicals formed from various compounds, including other organometallic compounds, and to measure the half-life period of such radicals. This, understandably, excited the chemical world because of the strong supporting evidence it gave to a deeply rooted concept which lacked only firm experimental support. We had a special interest in the work because it involved not only organometallic compounds, but more particularly because we believed and postulated that free radicals were intimately involved in the preparations, reactivity, and stability of organometallic compounds. When a question was raised early in such studies about the metallic mirror being picked up not by radicals but by hydrogen, I wrote Paneth suggesting that he might at that stage counteract that interpretation by picking up a mirror of a metal such as beryllium to form a relatively reactive organoberyllium compound (either dimethylberyllium or diethylberyllium) and so identify such RM compounds by appropriate derivatives and color tests. At his request, we sent him by ship very pure samples in glass ampoules which were unusually tightly sealed in metal containers to meet rather stringent transportation regulations. At first he had no success in picking up the beryllium metal. It appeared that the beryllium formed by pyrolysis of the dialkylberyllium compound may have entered into some sort of combination with silica in the reaction tube which prevented reaction with the alkyl radicals. Then, in an ingenious operation, a thin gold cylinder was inserted into the reaction tube; the beryllium metal was deposited on the gold sheet; the free methyl and free ethyl radicals picked up the beryllium; and the organoberyllium compounds were set down in the more remote, cooled parts of the tube.

We also had an additional illustration from that aspect of organometallic chemistry, on how unpredictable some reactions can be. Very shortly after the incidents just described, I learned from Gomberg that one of his graduate students prepared tetramethyllead incidental to an examination of the Paneth technique. While sealing the capillary of the partially filled glass ampoule holding the freshly prepared tetramethyllead, he had an unhappy accident, which fortunately did not result in serious personal injury. The whole of the tetramethyllead exploded, apparently due to an initial violent decomposition of an unobserved droplet in the capillary. I conveyed this information to Paneth, and asked if he or his students had made a like observation in their many experiments in pyrolyzing tetramethyllead. He informed me that none had occurred with  $\text{Me}_4\text{Pb}$  or  $\text{Et}_4\text{Pb}$ , but on one occasion tetrapropyllead had exploded.



## IX

### SOLVENT COORDINATION EFFECTS

In our early studies we observed with R. Jones and others, some significant solvent effects on coordination or "complex formation" as they influenced the reactivities of some organometallic compounds. They had been known for some time, and appeared rather striking when examined in connection with Michler's ketone and the color test. From our study it appeared that the order of decrease in relative reactivity and increase in tendency to form coordinate compounds with ketones was  $\text{PhLi}$ ,  $\text{PhMgBr}$ ,  $\text{Ph}_3\text{Ga}$ .

In some other studies on relative reactivities of organometallic compounds of the alkaline earth metals, it was observed that the decreasing order of relative reactivity was  $\text{R}_2\text{Ba}$ ,  $\text{R}_2\text{Sr}$ ,  $\text{R}_2\text{Ca}$ ,  $\text{R}_2\text{Mg}$ , and  $\text{R}_2\text{Be}$ . Incidentally in those studies it was noted that diethylzinc has a marked accelerating effect on some organometallic reactions. It was proposed that here the effect may be associated with the formation of coordination complexes.

The use of ethylenediamine to stabilize highly sensitive organogold compounds, and of TMEDA to augment the metalating activity of some  $\text{RLi}$  compounds has been mentioned elsewhere.

## X

### PHYSIOLOGICAL ACTION AND CHEMICAL CONSTITUTION

Over the years organometallic chemistry has played, and continues to play, an important part in studies concerned with physiological activity (14, 15, 30). Part of this is the role of any synthetically useful reagent. Also a number of organometallic compounds, such as mercurials, have been used directly in medicine. It is on this latter aspect we should like to mention briefly several of our studies. Some years ago in connection with research on organolead compounds, it occurred to us that it might be of assistance in throwing light on cancer therapy involving lead and some of its inorganic compounds, to prepare for pharmacological examination some organolead compounds. These studies point up the long-known pronounced effect of physical properties and of structure on the toxicity of several classes of compounds. With organolead compounds, it is known that the volatile tetraethyllead is quite toxic; and even the solid organolead halides of the

$R_3PbX$  type have the highly disagreeable physiological property of being active sternutators. However, marked alterations in pharmacological action can be effected by variations in structure.

One approach to the synthesis of some organolead dyes for therapeutic screening was first to introduce the *p*-aminophenyl group into an organolead compound, as we had done earlier with organophosphorus and organo-arsenic compounds. We soon found, for example, that complex mixtures were obtained from a reaction between triphenyllead chloride and *p*-aminophenyllithium (or its  $N-Li$  derivatives). The difficulty here probably resides in the metal-metal exchange reactions between organolead and organolithium compounds. However, because metal-metal exchange only occurs to a highly subordinated extent between  $RMgX$  reagents and organolead compounds, we first converted the  $RLi$  compound to the corresponding  $RMgBr$  compound by means of magnesium bromide.



The *p*-aminophenyllead compound (or more correctly its  $N-Li$  derivatives) was diazotized (with attendant conversion of  $N-Li$  to  $N-H$ ) by conventional procedures, despite the presence in the molecule of a supposed labilizing aminoaryl group. Coupling of the diazonium compound with  $\beta$ -naphthol, for example, gave an azo lead compound which was red in acid solution and green in basic solution. Reactions of this type provided the essential means for the introduction of water-solubilizing groups to vary the lipid-water distribution of the less chemically reactive organometallic compounds. Incidentally such a technique should be helpful for the optical resolution of some organolead compounds. Other approaches to organolead dyes containing water-solubilizing groups involved the prior formation (by means of suitable  $RLi$  compounds) of an  $R_3PbC_6H_4OH-o$  type, and then coupling of this (in the para position to the  $OH$ ) with suitable diazonium compounds.

In connection with the introduction of water-solubilizing groups we found that this could be realized effectively by formation of onium derivatives. As an illustration of another approach, triphenyl- $\gamma$ -diethylamino-propyllead (formed in 91% yield from  $\text{Ph}_3\text{PbLi}$  and  $\gamma$ -diethylaminopropyl chloride) gave by customary procedures the quaternary ammonium sulfate,

which was quite soluble in water. This suggested the conversion of triphenyl- $\gamma$ -diethylaminopropyllead, by means of dimethyl sulfate, to the corresponding methyl sulfate or methosulfate derivative. This compound was extremely soluble in water, apparently in any proportion, thereby disposing of a water-solubility problem.

Corresponding phenomena were observed with some organotin compounds. As an illustration, tetra-*p*-dimethylaminophenyltin when treated with methyl iodide gave a tetramethiodide which could be recrystallized from water; but the salt obtained from the reaction of tetra-*p*-dimethylaminophenyltin with dimethyl sulfate was too soluble in water to be purified from this solvent. In general, the solubility of these quaternary ammonium salts increases with an increase in the number of quaternary ammonium groups; and the methosulfates generally have a higher solubility than the corresponding methiodides.

Appropos tumor studies, investigations were carried out on an aspect of brain tumor therapy. It was known that some compounds containing the boron-10 isotope appeared promising in secondary irradiation of brain tumors. Among other types synthesized by us were variously substituted boronic acids containing hydroxyl groups which appeared to enhance the efficacy, and some appropriately substituted boronic dyes. The synthesis of most of these compounds was effected by use of organolithium compounds formed, in most cases, by halogen-metal exchange.

Relevant to organometallic and organometalloidal dyes, a wide variety of silicon-containing azo dyes was prepared. Among other properties, they were also tested for their lightfastness and their substantivity in comparison with silicon-free analogous compounds. Reference should be made here to the extensive studies by Voronkov on physiologically active organosilicon compounds. A broad category of organometallic compounds was examined for plant growth regulator action. In the extensive studies with Yale on organobismuth compounds (30) the pharmacological investigations were supplementary to the following aspects: metal-metal exchanges with new classes of organobismuth compounds, studies in liquid ammonia, color tests involving organobismuth compounds, and relative reactivity comparisons. New organogold compounds were prepared in connection with therapeutic studies on arthritis. More noxious compounds were prepared incidental to some World War II studies (mentioned later), as well as less toxic agents in fungicidal and insecticidal studies of both military and peacetime interest.

## XI SOME WORLD WAR II STUDIES

During World War II, a number of investigations were carried on which involved organometallic and organometalloidal studies. The following are a few selected items which did not include research concerned with anti-malarials, insecticides, etc. Very early in the war, and at a time before the Manhattan Project was formally established, we did work on organic compounds of uranium. These studies were undertaken to find compounds of uranium suitable for isotope separation. Of particular interest were substances of high volatility, high stability, and low molecular weight. Some prior work in our laboratory had already indicated that simple organometallic derivatives such as tetramethyluranium, if they existed at all, were highly unstable, and their isolation offered little chance of success. Therefore, attention was directed to the preparation of other types of organic compounds linked to uranium through oxygen, nitrogen, or sulfur atoms. Eventually a considerable knowledge of the organic chemistry of uranium evolved, and some relatively stable and volatile compounds were discovered. One of the more obvious approaches to finding volatile compounds appeared to be through preparation of chelate complexes with highly fluorinated 1,3-dicarbonyl reagents. During the course of this work, with the special help of some former students (particularly that of R. Jones) other more stable and more volatile compounds, especially the uranium(V) and uranium(VI) alkoxides, were prepared (25).

Another aspect of some organometallic chemistry involved the preparation of organotin compounds. This work was motivated largely by the potential increased availability to others of tin and some of its ores, in an early stage of the war, in parts of southeast Asia. In principle this was a so-called defensive operation, to prepare and examine organotin compounds as potential chemical warfare agents in order to learn how defensively to anticipate and to meet such exigencies as decontamination. Although some highly toxic organotin compounds were prepared, it is pleasant to recall that none was used.

Among a number of incidental studies was one of a potential anticipatory nature. Early in the war the need arose for some means of igniting oil on water. For this purpose it was felt desirable initially to be able to supply in several possible ways an ignitor of an oil spread on sea water, such as bunker oil, with a thickness of about  $\frac{1}{8}$  of an inch. This involved largely a review of compounds which we and others had prepared over the years and which

met three important conditions: (1) immediate ignition as a pyrophoric material, on exposure to air; (2) resistance to hydrolysis by water; and (3) low specific gravity. The organometallic compound which appeared (solely on the basis of deduction) to meet the requirements was triethylboron. Accordingly, some of the compound was prepared with R. Leeper (in later experiments in almost quantitative yields), and tests revealed that when the triethylboron was liberated under the surface of oil on water, it was possible to ignite oil with a thickness of  $\frac{1}{32}$  of an inch or less.

## XII

### SOME RECENT AND CURRENT STUDIES

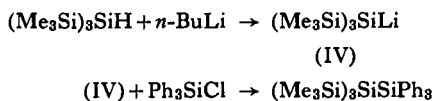
A part of the work in this section has not yet been published. Most of it has been done under the auspices of the United States Air Force, Materials Laboratory, on some basic aspects of high-temperature fluids and lubricants. We are deeply grateful to the U.S. Air Force for their support and co-operation.

#### *A. Mass Spectroscopy*

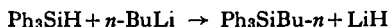
We have mentioned elsewhere that Kipping obtained from the reaction of diphenyldichlorosilane with sodium several compounds, among them three individual substances of the general formula  $(\text{SiPh}_2)_n$  designated by him as "Compounds A, B, and C." The identity of these three compounds was a subject of uncertainty, and only in recent years was the matter clarified. Thus, "Compound A," described by Kipping as a linear biradical species, was identified as octaphenylcyclotetrasilane. "Compound B" was described as a four-membered or as a six-membered ring compound, but now it is known as decaphenylcyclopentasilane. For "Compound C," a six-membered ring structure was suggested and supporting evidence was obtained. We have recently studied the mass spectra of "Compounds A, B, and C." Molecular ions were obtained for each of these substances which confirmed our previous structural formulations based largely on chemical transformations, particularly that of ring cleavage. In order to compare certain of the spectral features with a nonphenylated type, the spectrum of dodecamethylcyclohexasilane was measured. The major fragment ions in all four compounds are rearrangement ions resulting from phenyl or methyl migration. Fragmentation mechanisms and structures for the major ions have been proposed, using the many observed metastable ions as an aid.

### B. $d\pi$ - $d\pi$ Bonding

It has been reported that triphenylsilane reacts with some RLi compounds to give  $\text{Ph}_3\text{SiR}$ , whereas triphenylmethane and triphenylgermane yield the respective lithium compounds:  $\text{Ph}_3\text{CLi}$  and  $\text{Ph}_3\text{GeLi}$ . The disparity in the mode of reaction of these Group IV metal-hydrogen compounds with organolithium species has been explained in terms of the relative polarizations of the E—H bonds (E = C, Si, or Ge). We have recently observed an unusual metalation reaction involving tris(trimethylsilyl)silane (IV) and *n*-butyllithium. Treatment of (IV) with *n*-BuLi in an ether-tetrahydrofuran mixture gave a greenish-yellow-colored solution with gas evolution (butane). On derivatization of this solution with chlorotriphenylsilane, the major product isolated was tris(trimethylsilyl)(triphenylsilyl)silane.



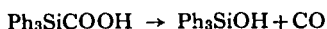
It is interesting that none of the coupling product tris(trimethylsilyl)-*n*-butylsilane was isolated. Under similar conditions, triphenylsilane reacts with *n*-butyllithium to give only *n*-butyltriphenylsilane.



The formation of  $(\text{Me}_3\text{Si})_3\text{SiLi}$  from the corresponding Si—H compound and *n*-BuLi may indicate that the hydrogen atom is more protonic than the hydrogen atom of triphenylsilane. This relatively greater acidity of the hydrogen atom in  $(\text{Me}_3\text{Si})_3\text{SiH}$  is probably associated with the nature and degree of dative  $\alpha$ -bonding. Due to the fact that the electrons around silicon are more polarizable (compared to carbon) the Si—H bond may be polarized in different directions under different conditions. In view of some other data, a radical mechanism might be tenable. That is, *n*-BuLi might act as an electron-donating agent towards the silicon compound to give a silyl radical anion which could lose a hydrogen atom to the butyl radical. It has been suggested (Eisch) that the steric crowding hinders access of the butyl anion to silicon; and the resultant radical anion is more stabilized because of  $d\pi$ - $d\pi$  delocalization than is the trisilyl anion because of  $p\pi$ - $d\pi$  dispersal. It might be mentioned here that previous attempts to prepare peralkylsilyllithium compounds under comparable conditions have failed, leading to the conclusion that  $(\text{Me}_3\text{Si})_3\text{SiLi}$  may be significantly stabilized by  $p\pi$ - $d\pi$  bonding.

### *C. Concerning Dissociation of Dimetallic and Dimetalloidal Species*

One aspect of our studies concerned with relationships between analogous compounds of silicon and carbon (22) was with analogs of hexaphenylethane, containing Group IVB elements other than carbon, in order to study the tendency of these compounds to dissociate into free radicals. After showing, with T. C. Wu, that none of a wide variety of disilanes exhibited dissociation, triphenylmethyltriphenylsilane was prepared and showed no tendency to dissociate into free radicals under conditions where the dissociation of hexaphenylethane is readily detected. In view of the general similarity of organogermanium and organosilicon compounds, it was therefore not unexpected to find that triphenylmethyltriphenylgermane,  $\text{Ph}_3\text{C}-\text{GePh}_3$ , was a similarly unreactive and stable compound showing no tendency to dissociate. These studies with A. Brook involved some interesting and novel syntheses, and also some unusual reactions growing out of cleavage of the central elements. The central bond can be cleaved by alkali metals to give metallic derivatives which when carbonated yield the respective carboxylic acids. These acids, such as triphenylsilanecarboxylic acid, and some derivatives, undergo base-catalyzed elimination reactions.



Complete decomposition of the pure acid, with evolution of carbon monoxide, occurs rapidly by treatment of the acid with only catalytic amounts of aqueous sodium hydroxide or sodium ethoxide in absolute ethanol, and more slowly with sodium methoxide in absolute methanol, or with aqueous pyridine. In each case the only products isolated from the reaction are carbon monoxide, liberated quantitatively, and triphenylsilanol. It appears that a nucleophilic attack by the base on the acid occurs, and that triphenylalkoxysilane, carbon monoxide, and hydroxyl ion are initially formed. This latter species then competes with the alkoxy ion for the remaining acid and, further, causes hydrolysis of the triphenylalkoxysilane already formed, so that only triphenylsilanol is isolated. The reactions may pass through a pentacovalent intermediate. The elimination of carbon monoxide under such mild conditions had not been observed in organic chemistry. The facility with which these decompositions occur is significant in that it clearly demonstrates the marked susceptibility of silanes bearing electron-attracting substituents to attack by nucleophilic reagents.

Related work is on the alkaline cleavage of tetrasubstituted silanes. Many investigations have been reported whose ultimate purpose has been to establish a general series by which the relative ease of cleavage of an organic radical from a metal could be predicted. While silicon is not generally considered to be a metal, it has been found to behave in a manner qualitatively analogous to metals in cleavage reactions. Although a comprehensive survey of the cleavage reactions of organosilicon compounds had not been made, numerous isolated examples by both acidic and alkaline reagents were reported, particularly of the various halogen- and oxygen-substituted alkylsilanes. We extended such investigations into the realm of alkaline cleavage of tetrasubstituted arylsilanes and mixed arylalkylsilanes, to attempt to correlate the ease with which a hydrocarbon fragment, such as a carbanion, was cleaved from silicon by the nucleophilic reagent with the acid strength of the parent hydrocarbon. We treated a number of tetrasubstituted arylsilanes and arylalkylsilanes with potassium hydroxide in various solvents under a variety of conditions, and ascertained the extent of cleavage, together in certain cases with the products formed by the cleavage. The greater susceptibility of a silicon atom to nucleophilic attack as compared with carbon in the corresponding carbon compound can be attributed to several factors. The larger size and extra electron shell of the silicon atom screen its nuclear charge and make it more polarizable than carbon. An electron-attracting group attached to silicon is able to withdraw electrons from the valence shell, inducing a positive charge on the silicon atom, thus making nucleophilic attack on the silicon atom more favorable. Furthermore, silicon, in contrast to carbon, is capable of expanding its valence shell to become penta- or hexavalent. Hence, a tetrasubstituted silane is able to form a more or less stable coordination complex with the nucleophilic reagent, and thus, any of the groups originally bonded to the silicon atom have a relatively greater chance of being expelled than if no such complex was possible. From such a mechanism it follows that electron-attracting substituents should increase the rate of the reaction, and further that the strongest electron-attracting substituent should be that which is cleaved by the hydrolysis. From the qualitative cleavage of silanes with standard alkaline reagents, it was possible to draw up a series listing the order of decreasing ease of cleavage of groups from the triphenylsilyl group. This series closely parallels the relative acid strength of the corresponding hydrocarbons, and hence tends to substantiate the proposed mechanism which suggests that the stronger the electron-attracting properties of a



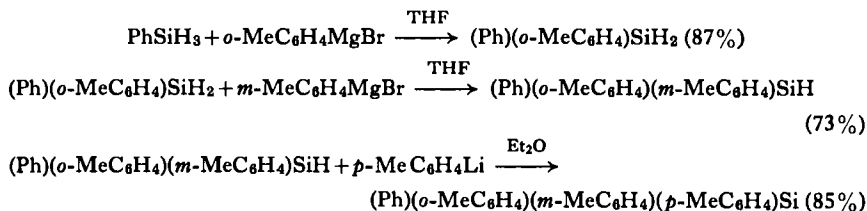
group (the more acidic the corresponding hydrocarbon), the greater will be its tendency to be cleaved by nucleophilic displacement. Cleavage reactions have been studied by many, and Eaborn particularly [to whom chemists are indebted for his classic text (7)] has made extensive kinetic studies of a variety of systems.

#### D. Asymmetrical Silicon in Organosilicon Compounds

The primary impetus for the development of some organometallic and organometalloidal types has been varied. It is interesting that studies concerned with the preparation and possible resolution of optically active isomers have played a significant role in a number of cases, particularly with organolead and with organosilicon compounds. The extended and beautiful work by E. Krause on organolead chemistry was motivated by his interest in this direction. In order to prepare initially an asymmetric molecule such as  $R^1R^2R^3PbX$ , it was necessary to build a chemistry of organolead compounds. It was relatively easy to prepare compounds such as  $R_4Pb$  and  $R_3PbX$ , but how to make a compound such as  $R^1R^2R^3PbX$ ? This involved a study in both breadth and depth to learn much of the techniques and operations for the stepwise attachment of different groups to a lead atom. Krause did this, and greatly enriched thereby our knowledge of organolead chemistry. Regrettably his primary objective of the preparation of an optically active organolead compound was not realized.

It may be quite fairly stated that Kipping was similarly motivated initially in his studies to prepare an optically active organosilicon compound. In this he was successful. It is interesting to note the effective and most significant studies by Sommer (42) in the area of stereochemistry and mechanisms.

Our interests in highly unsymmetrical organosilicon compounds were along other lines, and one incentive was the development of syntheses of unsymmetrical compounds with low melting points. A selected illustration is the synthesis of phenyl-*o*-tolyl-*m*-tolyl-*p*-tolysilane.



Essentially these useful selective reactions depend on a variation of solvents and different organometallic compounds. Most of the unsymmetrical compounds were either low-melting solids, viscous liquids or glasslike semisolids. These compounds were synthesized with relative ease, whereas the preparation of analogous unsymmetrical tetraarylmethanes is much more difficult, a good illustration of the facile substitution at silicon compared to carbon. These reactions also illustrate the availability of some solvents and organometallic compounds not accessible to Kipping. Incidentally we also developed qualitative tests for the degree of substitution of organosilicon hydrides, having one, two, or three R groups attached to SiH. Related to these studies are the syntheses with E. Zuech of a series of novel heterocycles. It is relevant in this connection to mention one compound in particular: 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline. This cyclic organosilicon compound was one of a series found to have useful additive properties for highly thermally stable lubricants. Other significant work in this area was done by C. Tamborski and his co-workers.

### *E. Noncatalyzed Disproportionation of Diphenylsilane*

Reactions of disproportionation or redistribution have long been known. Practically all such reactions observed in organosilicon chemistry have involved Lewis acids, which are known (3) to be highly effective catalysts. We observed that diphenylsilane undergoes a disproportionation reaction in the presence of a platinum catalyst or, most strikingly, in the absence of any added catalyst. The initial discovery was made during an attempt to add diphenylsilane to furan using chloroplatinic acid as the catalyst. The use of this catalyst for similar additions has been recommended by J. Speier. From a reaction in which diphenylsilane, with no added catalyst, was heated in a bath at 300°C, there were isolated:  $\text{Ph}_4\text{Si}$  (0.1%);  $\text{Ph}_3\text{SiH}$  (11.8%);  $\text{Ph}_2\text{SiH}_2$  (45%);  $\text{PhSiH}_3$  (11.2%); and only a possible very small quantity of  $\text{SiH}_4$  (which was shown to be present in some other reactions). Any close correlation with a random redistribution may have been fortuitous.

### *F. Silenes*

Some years ago we proposed divalent organosilicon compounds as reaction intermediates. More recently, in other studies, it seemed quite probable that the reaction of silacyclopentadienes under suitable Diels-

Alder conditions could provide access to the 7-silanorbornadiene ring system. In view of the unusual reactivity of norbornadienes in general we felt it would be of considerable interest to investigate the effects produced upon the introduction of silicon into this bicyclic system. In particular it was of special attractiveness to investigate the possibility of using the 7-silanorbornadienes as precursors to "divalent silicon" (silene) species. The thermal decomposition of compounds such as dimethyl and diphenyl derivatives generates dimethyl- and diphenylsilylene; one of the satisfactory trapping agents for these divalent silicon compounds is diphenylacetylene, which gave the corresponding disilacyclohexadienes. Prior to these studies was the work with D. Peterson on the diphenylsilylene moiety, incidental to his investigations on silylmetallic compounds.

### *G. Small-Ring Organosilicon Compounds*

The highly reactive nature of Kipping's "Compound A," octaphenylcyclotetrasilane, prompted an investigation into the chemistry of other four-membered silicon-containing heterocycles. There were synthesized, in studies with W. H. Attwell, 1,1,2-triphenyl-1-silacyclobutane and 1,1,2-triphenyl-1-silacyclopentane, in order to compare the reactivities of these two compounds. The five-membered ring was found to be quite unreactive under conditions where the four-membered ring was readily cleaved. Mechanisms involving *d*-orbital participation should be operative in cleavage of both compounds. The observed difference in reactivity between the two cyclic compounds can be explained in part by a qualitative consideration of both the ground and the transition state energies. In view of the apparent distortion of bond angles resulting in the formation of a considerably strained ring system, the silacyclobutane should possess a more energetic ground state than its ring homolog to favor ring opening of the former. Two of the several reactions studied are of particular interest. One was the cleavage of the cyclobutane ring by lithium aluminum hydride; the other was the exothermic opening of the cyclobutane ring on an alumina column, a reaction which we found to be most fruitful in establishing the structure of decaphenylcyclopentasilane subsequent to its initial opening.

A pseudo-silacyclobutene derivative, 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene, was prepared by three independent synthetic procedures, and was found to exhibit the high reactivity of silacyclobutanes. The facile ring openings observed with this pseudo-silacyclobutene are

readily explained in terms of the factors contributing to the reactivity of the silacyclobutanes.

Comparisons were made of the relative reactivities of 1,1,2-triphenyl-1-silacyclobut-2-ene and 1,1,2-triphenyl-1-silacyclopent-2-ene. Here, also, the four-membered ring was found to be more reactive. However, one of the most unexpected properties of the silacyclobutene was its inertness to  $\text{>C=C<}$  hydrogenation, in contrast to its five-membered ring homolog. Incidentally, the main difficulty involved in the preparation of a silacyclobutene is the susceptibility of the four-membered silicon rings to nucleophilic ring opening. Thus, a great majority of the known dehydrohalogenation techniques are of little use. The successful synthesis of our silacyclobutene involved the treatment of 2-bromo-1,1,2-triphenyl-1-silacyclobutane with an ether solution of phenylmagnesium bromide.

#### H. Ultraviolet Spectra Studies

Interesting observations have been made on the ultraviolet spectra of the small-ring organosilicon and other compounds in our various studies. However, only a few selected items will be mentioned here.

It was suggested that the unique ultraviolet spectral properties of hexaphenyldisilane were due to an intense interaction between phenyl groups which is facilitated by a type of interaction involving overlap of vacant *d* orbitals on silicon. Prompted by this observation, we examined a number of compounds incidental to our expanding polysilane studies in the series,  $\text{Ph}(\text{SiMe}_2)_n\text{Ph}$ , where  $n=2-6$ . The successive interposing of dimethylsilylene units between the phenyl groups should effectively diminish the interaction between the phenyl groups. However, quite the opposite was observed and the behavior noted can be considered to be analogous to the properties of the  $\alpha,\omega$ -diphenylpolyenes. This implied that the polysilane chain itself might absorb ultraviolet radiation without the presence of phenyl groups. We investigated the ultraviolet properties of the family of permethylated straight-chain polysilanes,  $\text{Me}(\text{SiMe}_2)_n\text{Me}$ , and found that they do in fact possess characteristic ultraviolet spectra. The position of maximum absorption and the molar absorptivity increase quite regularly with increasing chain length, a property which is observed with other linearly conjugated systems. In general, the molar absorptivity in this series of compounds increases with the increasing number of phenyl groups and with optimum conjugation across the silicon-silicon bond. The positions

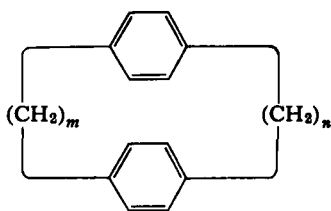
of absorption maxima tend to follow the same order; however, there are some discontinuities because the conjugation of vicinal phenyl groups has greater influence than the addition of phenyl groups in a geminal position. It is apparent that the unique spectral properties of polysilanes are due to the silicon-silicon bond acting as a chromophore, probably through the use of vacant  $d$  orbitals of the silicon atom. Substituents such as phenyl and vinyl with their  $\pi$ -electron systems are apparently able to be conjugated with polysilane chains through suitable overlap of  $d$  and  $\pi$ -orbitals.

An examination was also made of the ultraviolet properties of the perphenylated linear polysilane series,  $\text{Ph}(\text{SiPh}_2)_n\text{Ph}$  (where  $n=2$  through 7). The characterization of this series presented a difficult problem when the usual analytical, spectral, and chemical methods were employed. It is, however, now clear that the ultraviolet properties of a given homologous polysilane series can give direct and highly useful information concerning the length of the Si chain. A comparison of the data on members of this series with those obtained for the analogous permethylated polysilane series,  $\text{Me}(\text{SiMe}_2)_n\text{Me}$ , illustrates the large bathochromic shifts associated with phenyl substitution. In addition, the increased complexity of the spectra with increasing chain length is consistent with the  $\text{Me}(\text{SiMe}_2)_n\text{Me}$  series. Since the ultraviolet spectral properties have been associated with the Si-Si chromophore, the bathochromic shift observed with  $(\text{SiPh}_2)_4$  may be a reflection of the increased ground state energy of this molecule resulting from internal strain.

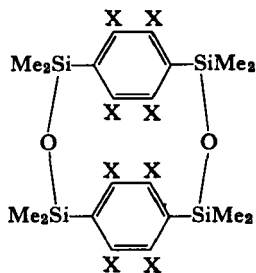
In connection with our studies on polyhalogen types, examinations have been made of the ultraviolet spectra of  $\alpha,\omega$ -bis(pentachlorophenyl)-permethylated polysilanes,  $\text{C}_6\text{Cl}_5(\text{SiMe}_2)_n\text{C}_6\text{Cl}_5$  (where  $n=1$  through 6). Here, in contrast to the analogous diphenyl compounds, the pentachlorophenyl-substituted permethylated polysilanes show little variance in the wavelength of maximum absorption with increasing silicon chain length. The molar absorptivities do vary with chain length, however, and are abnormally high. Among other compounds examined were  $\text{C}_6\text{F}_5(\text{SiMe}_2)_n\text{C}_6\text{F}_5$  (where  $n=1$  or 3). Since the increase of the electronegativity of the substituent in the benzene rings so drastically affected the spectra, an examination was made of a series of compounds  $p\text{-XC}_6\text{H}_4(\text{SiMe}_2)_2\text{C}_6\text{H}_4\text{X-p}$  (where  $\text{X}=\text{Cl}, \text{Br}, \text{SiMe}_3$ , and  $\text{NMe}_2$ ). It was found that the position of absorption attributed to the Si-Si bond chromophore shifted to longer wavelengths, and a considerable increase in molar absorptivities occurred with the four compounds. Thus the conjugation existing in the unsubstituted

diphenylsilane has been increased due to the substituents in the benzene rings, the least change occurring with the most electronegative substituent.

Along the lines just mentioned, we synthesized, with I. Haiduc, perhalogenated analogs of paracyclophanes (V) with disiloxanyl bridges linking the aromatic rings, namely, perchloro- and perfluorocyclobis(*p*-phenylenetetramethyldisiloxanes) (VI).



(V)



(VI)

a, X = Cl; b, X = F

The B bands of the cyclic compounds (VIa) and (VIb) exhibit the most dramatic bathochromic shifts, thus suggesting that the deformation of the aromatic nuclei and some transannular interaction of the two aromatic rings is a feature which persists also in the disiloxane-bridged polyhalo-aromatic derivatives of type (VI). The replacement of chlorine for fluorine atoms in the aromatic nuclei also has a pronounced effect upon the ultra-violet absorption spectrum, resulting in a broadening of the B band, disappearance of the fine structure and a strong hypsochromic effect upon the band.

### 1. Silylmetallics

The first authenticated preparation of a silylmetallic compound was due to the very attractive work by Benkeser. Thus triphenylsilylpotassium was formed together with  $\alpha,\alpha$ -dimethylbenzylpotassium by cleaving  $\alpha,\alpha$ -dimethylbenzyltriphenylsilane with sodium-potassium alloy in ether. However, the preparation was not a very useful route to the silylmetallic reagent since a reactive organometallic compound was also present in the reaction mixture. In the same year appeared the first of an extensive series of papers by us describing the formation (generally by direct cleavage of a

disilane), and reactions of silylmetallic compounds. Reviews in this area have appeared with Wittenberg (44) and with Winkler (28). These silylmetallic compounds have a degree of reactivity and a versatility of reaction that equals or exceeds in many cases some of the more conventional synthetic agents: the Grignard and the organolithium compounds. In the course of developing this highly fruitful area of chemistry, synthetic and theoretical, we have carried out a wide series of studies. These have involved, among some fundamental operations, an examination of optimal conditions for preparation in studies with G. Lichtenwalter and others; relative stabilities in a variety of solvents; qualitative and quantitative analyses; and comparative reactivities with some other metallic species, including metallic derivatives of Group IVB elements, having germanium or tin or lead in place of silicon, etc. In the silylmetallic compounds, the metal has varied widely; and within the year satisfactory directions have been reported for the sodium derivatives which hitherto have been relatively inaccessible and which provide a greater spread of selective reactivity. The "R groups" attached to Si—M can be varied quite widely, and a few of them have been referred to briefly in this account, namely, compounds such as  $(\text{Me}_3\text{Si})_3\text{SiLi}$ ,  $(\text{HMe}_2\text{Si})_3\text{SiLi}$ , and  $\text{Li}(\text{SiPh}_2)_4\text{Li}$ .

### *J. Organometallic Compounds of Copper, Silver, and Gold; Thermal Stabilities*

A chief purpose of this section is to compare the thermal stabilities of some organometallic compounds. Many years ago in some studies of organometallic compounds of copper, silver, and gold, we made some generalizations on their relative thermal stabilities. In the reaction of cuprous salts with methyllithium two products were formed. One of these,  $(\text{MeCu})_n$ , was ether-insoluble; the other,  $\text{LiMe}_2\text{Cu}$ , was ether-soluble. The  $(\text{MeCu})_n$  underwent a violent explosion when dried and exposed to the air. Trimethylgold was prepared with Woods from gold tribromide and methyllithium. We found that even its ethylenediamine complex was not only light-sensitive, but exploded violently on warming. Before the trimethylgold itself was prepared the general observation was made by several of the "impossibility of existence of a trialkylgold." This was altogether reasonable in view of prior experiments, and of the very low thermal stability we observed for the compound. It has been noted (40) that this was "the first 'normal' liquid of a transition metal to be made."

Some of the simple generalizations we made then on the order of decreasing thermal stabilities were as follows:

- (1)  $\text{PhCu} > \text{PhAg} > \text{PhAu}$
- (2) Alkyls:  $\text{Cu} > \text{Ag} > \text{Au}$
- (3) Aryl  $>$  Alkyl

As mentioned in this general section, our interest has turned to organometallic and organometalloidal compounds of increased thermal stability. With this in mind we are examining the introduction of groups that give high promise of enhancing thermal stabilities in both monomers and polymers. Highly fluorinated and highly chlorinated groups are known to be in this category. It is expected that substituents such as pentafluorophenyl, pentachlorophenyl, and tetrachloropyridyl would be interesting in this connection. One way of introducing them is via their organocopper compounds. We have found that a compound such as pentafluorophenylcopper is markedly more stable than its nonhalogenated counterpart, phenylcopper, and yet is reactive enough to permit its use for the introduction of the pentafluorophenyl group. We might mention that one of the ways of preparing the pentafluorophenylcopper is via the lithium dimethylcopper,  $\text{Li}^+(\text{Me}_2\text{Cu})^-$ . As an added evidence of how new applications of old compounds turn up, we might mention here the very recent work by Corey (5) of a particularly effective and promising methylation process using the  $\text{LiMe}_2\text{Cu}$ .

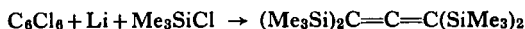
It should be mentioned that there is a very wide range in thermal stabilities among organometallic compounds, and thermal stability appears to have little discernible relation to "chemical reactivity." Actually W. Carothers reported many years ago that the highly reactive methylsodium and methylpotassium begin to decompose at room temperature, and that such decomposition of methylpotassium is very appreciable at 50° C. Among the less reactive organometallic compounds are the mercurials. Here we found to our regret that they ill-served a purpose of reference derivatives. This was related to the comprehensive studies with G. F. Wright on the important mercuriation reactions of some highly sensitive furans. These mercurials were excellent and necessary for numerous transformations but they could hardly be set aside with confidence as reference derivative samples, for anything like the 20-year period over which we found ether solutions of  $\text{MeMgI}$  to be essentially unchanged. With organosilicon compounds, which generally are of a low order of reactivity, we found with R. K. Ingham and others that some of them have high thermal stability.



### *K. Reactions with Perhalogenated Types*

We have referred occasionally to some current studies involving polyhalogen compounds, particularly those containing chlorine or fluorine. We shall restrict our consideration, because of space limitations, to a segment of what may be termed polytrimethylsilylation reactions.

We have observed that when hexachlorobenzene is treated with an excess of lithium and chlorotrimethylsilane an unusual reaction occurs with the formation of tetrakis(trimethylsilyl)allene as the major product.

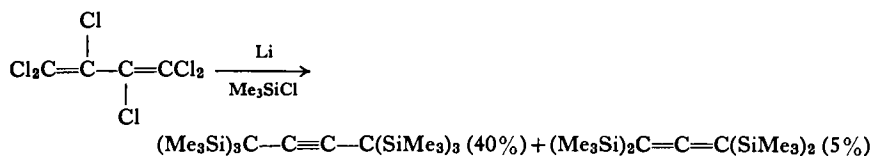


This compound was first prepared in some noteworthy studies by R. West from tetralithiopropyne and chlorotrimethylsilane. We have observed the formation of the allene from reaction of lithium and chlorotrimethylsilane with a great variety of polyhalogenated compounds. The diversity of transformations is very large, and the number of exceptional reactions is also great.

In some reactions involving Li and  $\text{Me}_3\text{SiCl}$ , as with pentachlorophenyltrimethylsilane, the yield of the allene is in excess of 50% on the basis of two allene molecules deriving from one polysubstituted benzene. However, the allene is also formed from a cycle with only five carbon atoms; such as pentachloropyridine. Furthermore, the yield of allene from a simple linear compound such as hexachloropropene is in excess of 75%.

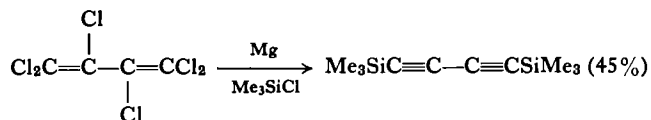
With the great variety of polyhalogenated compounds, containing varying numbers of fluorine, chlorine, and bromine atoms; and with the heterogeneity of the several reaction systems; and with a variety of metals in place of lithium, it is to be expected that no single mechanism may be operating. One simple intermediate that is reasonable is tetralithiopropyne. Another possible intermediate is trimethylsilyllithium. This is postulated because of the reactions of  $\text{R}_3\text{SiLi}$  compounds with some polyhalogenated types of compounds. Depending on the reactants, it appears that carbenoid and cyclopropenoid types, benzyne structures, and anion radicals may be involved, as indicated in some of our current work.

As an evidence of the complexity and novelty of some of these transformations we might mention a current study on the reaction of hexachlorobut-1,3-diene with some metals and chlorotrimethylsilane. When the metal is lithium, two of the products so far isolated and identified are hexakis(trimethylsilyl)but-2-yne, and tetrakis(trimethylsilyl)allene.



Cleavage of a carbon-carbon bond to go from a four-carbon to a three-carbon system was unexpected. Also the properties of the hexa(trimethylsilyl)butyne are unusual. First, this compound has a high degree of thermal stability; second, the acetylenic linkage is uncommonly resistant to conventional (and some unconventional) addition reactions, probably because of steric factors.

When the same hexachlorobutadiene is treated with chlorotrimethylsilane and magnesium (in place of lithium) one of the products formed is 1,4-bis(trimethylsilyl)buta-1,3-diyne.

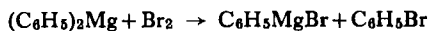


### XIII

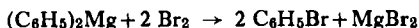
#### WHAT CONSTITUTES DISCOVERY?

There was a time when organometallic compounds were considered to have their beginning in 1849 with the discovery of diethylzinc by Frankland. In a series of classic investigations with inflammable and poisonous compounds, he extended his studies to other metals and soon laid the groundwork of much of our present knowledge of organometallic chemistry. In recent years some chemists feel the need of a redefinition of organometallic compounds. A part of this problem revolves about what constitutes a metal. Some time after we reported our experimental work of an historical nature on the first preparation of an organomagnesium compound, it seemed of interest to examine the products of some indefinite mercuration reactions to learn whether an organomercury compound may not have been prepared prior to 1849. We soon abandoned the idea when we became aware that chemists were considering the even earlier known organic arsenic compounds as belonging to organometallic chemistry. The field has broadened appreciably, but fortunately it has not reached the ultimate by accepting the thesis of some that carbon has some metallic characteristics: a definition which might classify simple hydrocarbons such as ethane and benzene as organometallic compounds.

Our experimental work of an historical nature to which we just referred concerns a study by H. Fleck which he reported in 1893. He purposefully set out to prepare phenylmagnesium bromide (by the slow addition of bromine to dry diphenylmagnesium covered with anhydrous ether) by the following reaction written by him:



However, because he obtained only bromobenzene and magnesium bromide he pictured the course of the reaction as follows:



and wrote, "One may assume that the latter reaction took place and that a stable compound corresponding with the formula  $\text{C}_6\text{H}_5\text{MgBr}$  was not formed." On the basis of some studies we had been carrying on at that time with  $\text{R}_2\text{Mg}$  compounds, it appeared altogether reasonable that phenylmagnesium bromide was an intermediate compound. We showed that Fleck did synthesize phenylmagnesium bromide as an intermediate step in his reaction. It must be remembered that he added an excess of bromine to the diphenylmagnesium, but he added it slowly, and sometime in the course of the addition there was present in the reaction mixture one molecule or one equivalent of bromine in accordance with the first reaction he postulated. We showed also that his second reaction was correct when an *excess* of bromine is added, inasmuch as almost exactly *two* molecules of bromine react with one molecule of diphenylmagnesium to give a solution which contains neither diphenylmagnesium nor phenylmagnesium bromide. What he did, therefore, was to first form phenylmagnesium bromide, and then destroy it by continuing the addition of bromine to an excess. His was probably the first reported reaction in which an organomagnesium halide is formed in ether. We are not concerned here with any consideration of his priority. He actually synthesized unknowingly the first organomagnesium halide; he knowingly set out to do so; but he equally definitely stated that a stable organomagnesium halide had not formed. Whatever earlier work was done by others does not detract from the splendid and comprehensive studies by Grignard (13). It is interesting to note that Grignard's grandson is doing industrial research in this country in the area of organometallic chemistry, and with not a little of his effort being with the remarkable reagent given to chemistry by his illustrious grandfather.

Another item in organometallic chemistry with some historical overtones concerns the well-known Zerewitinoff reaction or procedure for the

quantitative estimation of active hydrogens by the measurement of evolved methane. In this case T. Zerewitinoff published that his preceptor L. A. Tschugaeff first suggested  $\text{RMgX}$  for qualitative and quantitative analysis of hydroxyl types; suggested the use of pyridine as solvent; suggested that the work be undertaken by Zerewitinoff, as was done initially under his guidance; and that accordingly the procedure should be known as that of Tschugaeff-Zerewitinoff. As it turned out chemists would have little or none of this gracious recommendation by Zerewitinoff. In this case, can the problem be associated with a certain degree of inertia related to spelling? I understand there are more than seventy variants in the spelling of Mendeléeff.

One other item of historical interest may suffice. Paneth was an inorganic chemist who reported on simple free alkyl radicals, which he generated by the pyrolysis of alkylmetallic compounds of metals such as lead and whose half-life period he measured. About 3 years before, H. Taylor (a physical chemist) published in a less generally used periodical, his ideas and experimental observations on studies concerned with catalytic reduction processes of hydrogen-ethylene mixtures. He wrote that the simplest method of liberating free alkyl radicals into a mixture of these gases was by decomposition of metal alkyls such as diethylmercury and tetraethyllead.

The designation of the major research interests of these and other chemists who worked in this area serves to emphasize how great is the change which has taken place in recent years in the field of organometallic chemistry. Today there are no sharply defined areas of chemistry. The somewhat artificial barriers of some years ago have broken down. Many of the more noteworthy developments are coming from related and even disparate fields. This interplay of interests and the extension to areas which may not have been in the minds of researchers in their original studies has done very much for the whole of chemistry and related fields. It would be invidious to draw comparisons, but it may be said that no segment of chemistry exceeds organometallic chemistry in touching so extensively and so intimately on other areas, both basic and applied.

## XIV EPILOGUE

We have tried to convey in this cursory account some of the revolutionary changes which have occurred in organometallic chemistry, and the impact

of organometallic chemistry on other branches of science. The vignettes or episodes portrayed cover a span of more than 50 years of teaching and research. Whatever special merit our contributions may have is associated with a group effort provided by an uninterrupted cooperation with students. They supplied much inspiration and a reciprocal enthusiasm without which the extensive researches would have been impossible.

It is an uncommon experience to have been associated with the marked growth and development of one research area for so long a time. We are indebted to very many scientists who helped lay the groundwork over an extensive span of years. We have built on this rich heritage by supplementing it in breadth and depth to provide new, improved tools and techniques, as well as experimentally based useful generalizations and fundamental concepts of both academic and industrial significance. If history teaches us anything it is that contemporaries and those who come on the scene later can be depended upon to add appreciably to the imposing present structure. May they, too, have the joy and satisfaction that come with a continuing and broadening quest.

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# ***Oxidative-Addition Reactions of $d^8$ Complexes***

JAMES P. COLLMAN<sup>1</sup>

Department of Chemistry,  
University of North Carolina  
Chapel Hill, North Carolina

WARREN R. ROPER

Department of Chemistry,  
University of Auckland  
Auckland, New Zealand

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<sup>1</sup> *Present address:* Department of Chemistry, Stanford University, Palo Alto, California.



## I

## INTRODUCTION

The rapid development of organo-transition-metal chemistry over the past decade has been dominated by considerations of bonding and structure. The *reactions* of such organometallic compounds have been discussed to a lesser extent and usually in the context of a particular metal or ligand. Recent interest in homogeneous catalysis of organic processes by transition metal complexes has stimulated investigations of the reactions of organo-metallic compounds (29).

Chemists have long found it qualitatively useful to correlate organic chemistry by organizing reactions into patterns of mechanistically related transformations. Reaction patterns are now emerging from transition metal chemistry which can be systematized by a functional group approach similar to that used in organic chemistry. One such class of reactions involves oxidative additions whereby complexes of metals having a  $d^8$  electronic configuration are converted into octahedral complexes having a  $d^6$  configuration through addition of a covalent molecule (hereafter referred to as the addendum). These reactions can be further subdivided according to whether four-coordinate or five-coordinate  $d^8$  complexes are involved; different mechanisms may operate in the two cases. This review

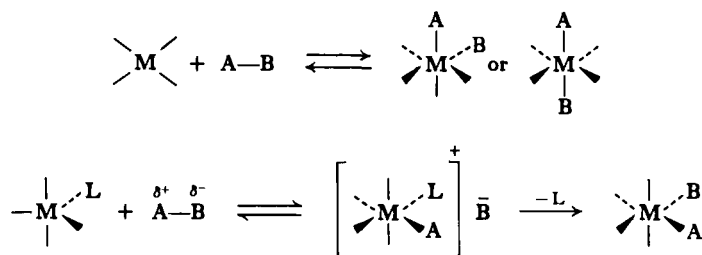


FIG. 1.

attempts to correlate oxidative-addition reactions of Group VIII complexes having a  $d^8$  configuration.

Addition reactions of coordinatively unsaturated, planar  $d^8$  complexes (Fig. 1) are often reversible and seem to be one-step processes. The behavior of  $d^8$  complexes in such reactions has been compared with that of carbenes (65). Depending on the conditions and the addendum (A—B) both *cis* and *trans* modes of addition have been reported (see Section II,B). Com-

pounds with both polar and nonpolar bonds react with unsaturated  $d^8$  complexes. Examples include oxygen, olefins, acetylenes, hydrogen, nonmetal hydrides, hydrogen halides and other protonic acids, metal halides, alkyl halides, acyl halides, halogens, and pseudohalogens. In certain cases (e.g., oxygen) addition takes place so that the two parts of the addendum (A—B) remain joined by a bond.

The apparent parallel between oxidative addition of covalent molecules to unsaturated  $d^8$  complexes and chemisorption of these molecules to the latent valences on transition metal surfaces may be significant. Several organic reactions that are homogeneously catalyzed by unsaturated  $d^8$  complexes involve oxidative addition as a key step in the mechanism. These include hydrogenation, hydroformylation, and dimerization of olefins (see Section VI).

Five-coordinate  $d^8$  complexes are coordinatively saturated and usually have a trigonal bipyramidal configuration (92, 95). These complexes add only polar or electrophilic molecules such as hydrogen halides and other strong acids, alkyl halides, mercuric halides, halogens, and perfluoroalkyl iodides. These oxidative-addition reactions take place in two discrete steps (Fig. 1), the second step being irreversible and resulting in the loss of a neutral ligand such as CO. The final products are usually those resulting from overall cis addition. The relationship between acid-base and oxidation-reduction reactions is particularly clear in the first step of this reaction. This behavior of the saturated  $d^8$  complexes has been compared with that of olefins (65).

An alternative pathway for five-coordinate complexes to undergo oxidative additions is through prior dissociation of a ligand to form a more reactive four-coordinate complex. Labilization of a ligand may be brought about by heating or irradiating a five-coordinate complex. For this reason certain reactions of five-coordinate  $d^8$  complexes require photolytic or thermal stimulation. An example is the hydrogenation of olefins catalyzed by  $\text{Fe}(\text{CO})_5$  above  $180^\circ\text{C}$  (59, 60, 61).

The definition of oxidation state used herein is the charge left on the central metal after the ligands have been removed in their "normal" closed shell configurations. Inasmuch as this definition is based on valence-bond formalism, there are several instances of indefinite oxidation state (see Section III). It is recognized that oxidation state is not a measurable physical quantity. However, the concepts of oxidation state and  $d$ -electron configuration which are used throughout this chapter are generally useful

accounting methods and provide a framework for organizing transition metal chemistry.

The tendency for  $d^8$  complexes to undergo oxidative additions depends markedly on the nature of the central metal ion and the ligands attached to it. The thermodynamic driving force of these reactions follows the familiar pattern of Group VIII chemistry (96). The tendency for  $d^8$  complexes to form oxidized adducts of  $d^6$  configuration increases upon descending a triad or passing from right to left within Group VIII (Fig. 2). Thus it is easier to oxidize Pt(II) to Pt(IV) than Ni(II) to Ni(IV) and easier to oxidize

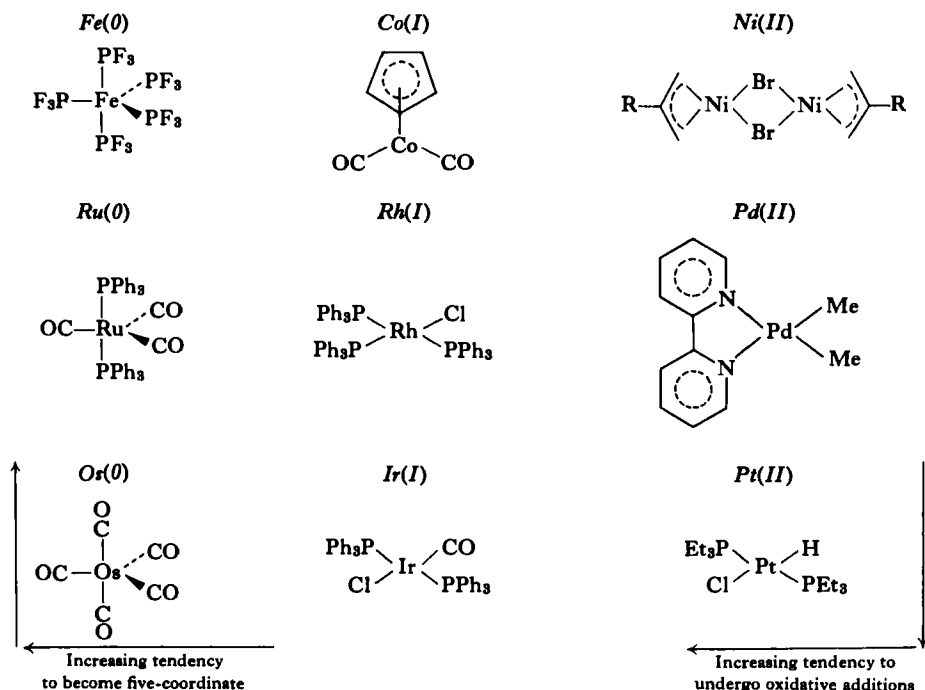


FIG. 2. Group VIII complexes with a  $d^8$  configuration.

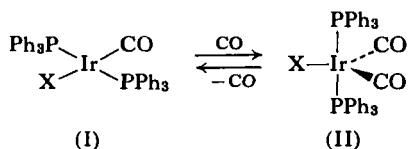
Os(0) to Os(II) than Pt(II) to Pt(IV). Because the ligands strongly influence the reactivity of  $d^8$  complexes (see Sections IV and V) it is difficult to make direct comparisons of reactivity except between isostructural compounds within a single triad. Ligands which increase electron density at the central metal enhance the tendency of the metal to undergo oxidative addition (21). Examples of this generalization are to be found throughout this review.

Typical complexes of Group VIII metals with a  $d^8$  configuration are presented in Fig. 2.

Meaningful comparisons between the kinetic reactivity of four- and five-coordinate complexes cannot be made because their oxidative-addition reactions proceed by different mechanisms. However, the general thermodynamic tendencies to become oxidized (Fig. 2) remain valid.

Because of the basic difference between the mechanisms by which unsaturated and saturated  $d^8$  complexes undergo oxidative additions it is necessary to consider the tendencies of Group VIII metals to form four- or five-coordinate complexes. Nyholm (95) has pointed out that in general the tendency for an element having a  $d^8$  configuration to become five-coordinate increases as one ascends a triad and as one passes from right to left in Group VIII (see Fig. 2). This generalization is illustrated by the pronounced tendency of iron(0) complexes to be five-coordinate whereas platinum(II) complexes are usually four-coordinate. The relative ease with which  $\text{Os}(\text{CO})_5$  loses a CO group compared with  $\text{Fe}(\text{CO})_5$  is another example of this point.

Planar  $d^8$  complexes are capable of forming a maximum of three  $d_\pi$  backbonds with the ligands. Taking the  $x$ - $y$  plane as the molecular plane,  $d_{xz}$ ,  $d_{yz}$ , and  $d_{xy}$  orbitals can take part in such  $\pi$ -bonding. On the other hand trigonal bipyramidal  $d^8$  complexes can form a maximum of four  $d_\pi$  backbonds using  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$ , and  $d_{(x^2-y^2)}$  (taking the apical positions as points along the  $z$  axis). In the presence of effective  $\pi$ -acceptor ligands an increase in electron density at the central metal will favor the formation of a five-coordinate complex. The influence of soft ligands on the coordination number of  $d^8$  complexes is illustrated by the equilibria between the planar complexes (I) and the trigonal bipyramidal complexes (II).



In the case  $\text{X} = \text{Cl}$  the planar complex (I) ( $\text{M} = \text{Ir}$ ) is the more stable form although the dicarbonyl complex (II) ( $\text{M} = \text{Ir}$ ) can be made under CO pressure (118). The iodide complex ( $\text{X} = \text{I}$ ) is stable in the dicarbonyl form (II) at room temperature and must be heated to remove CO (43). The hydride ( $\text{X} = \text{H}$ ) is much more stable as the pentacoordinate dicarbonyl

complex (43). This stabilization of five-coordinate complexes by soft ligands is undoubtedly the basis for the trans effect of ligands such as hydride in nucleophilic ligand displacement reactions involving four-coordinate platinum(II) complexes.

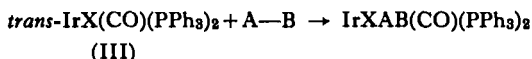
In Section IV oxidative-addition reactions are grouped according to the reagent (addendum) rather than the metal, the ligands, or the coordination state. This organization helps to emphasize the generality of the concept. It will become obvious to the reader that many examples of oxidative additions remain to be explored. The authors hope that this chapter will stimulate future work in this area. In view of the broad scope of this topic it is inevitable that some examples have been overlooked.

## II

### MECHANISMS

#### A. Kinetic Studies

Chock and Halpern (28) carried out the first kinetic study of oxidative-addition reactions of the remarkable iridium(I) complexes (III).



Each reaction was found to obey a second-order rate law:  $\text{rate} = k_2[\text{IrX(CO)(PPh}_3)_2][\text{A—B}]$ . Two reactivity patterns were observed, one for addition of hydrogen and oxygen and a different one for the addition of methyl iodide. This is not surprising since hydrogen and oxygen form adducts by cis addition, whereas methyl iodide adds in a trans manner (see Section II,B).

The rates of these reactions are strongly influenced by the nature of the halide ligand X and the solvent. For example, the rate at which methyl iodide adds to (III) follows the order  $\text{Cl} > \text{Br} > \text{I}$ . The reaction with methyl iodide is much faster in dimethylformamide than in benzene. For example, the rate of methyl iodide addition to the chloride complex at 30° C in dimethylformamide is nearly 17 times faster than the same reaction in benzene. The activation parameters for the methyl iodide reactions are in the range  $\Delta H^\ddagger = 5.6$  to  $8.8$  kcal/mole and  $\Delta S^\ddagger = -43$  to  $-51$  e.u., and reveal a pronounced solvent dependence. The large negative entropies of activation and the solvent dependence resemble parameters obtained from the reactions of tertiary amines with alkyl halides which go through a highly polar

activated complex (28). It was suggested therefore that the alkylation of the iridium complexes be considered as a bimolecular displacement ( $S_N2$ ) reaction at carbon in which the iridium atom acts as a nucleophile. This idea finds additional support in the qualitative effects of changing the phosphine ligands (see Section IV,E).

The rate constants for addition of oxygen and hydrogen to the iridium(I) complex show a different dependence on the halide ion:  $I > Br > Cl$  (28). In benzene the activation parameters for these reactions are in the range  $\Delta H^\ddagger = 10.8$  to  $13.1$  kcal/mole and  $\Delta S^\ddagger = -14$  to  $-24$  e.u. The large negative entropy of activation was interpreted as evidence for a highly constrained or ordered activated complex. It is interesting that the iodide oxygen adduct  $IrI(O_2)(CO)(PPh_3)_2$  is more stable than the corresponding chloride complex  $IrCl(O_2)(CO)(PPh_3)_2$  (90) and their relative rates of formation are about 10:1. Structural differences between these oxygen adducts are discussed in Section III,A.

Addition of deuterium to  $IrCl(CO)(PPh_3)_2$  shows only a small kinetic isotope effect,  $k_H/k_D = 1.22$ , suggesting little H—H bond breaking in the activated complex (22). Considering the high energy of the H—H bond, cis addition, a large negative entropy of activation, and the small deuterium isotope effect, a reasonable formulation of the mechanism is a concerted insertion of the iridium atom into the H—H bond. It is implied that the equilibrium constant for the formation of the hydrogen adduct,  $K = [IrX(H)_2(CO)(PPh_3)_2]/[IrX(CO)(PPh_3)_2][H_2]$  is larger for  $X = I$  than for  $X = Cl$ . This is consistent with the effect of soft ligands on the capacity of  $d^8$  complexes to combine with hydrogen (see Section IV,A).

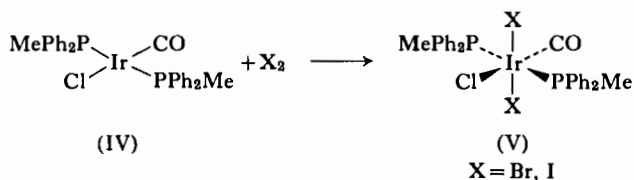
## B. Stereochemistry

### 1. Additions to Four-Coordinate Complexes

Oxygen and hydrogen react with the iridium(I) complexes, *trans*- $IrX(CO)(PPh_3)_2$ , to form cis adducts. The structures of the oxygen adducts have been determined by X-ray diffraction (72a, 81, 90) (see Section III,A). The cis configuration assigned to the hydrogen adducts is supported by NMR and infrared spectra (see Section IV,A) (21, 62, 109, 122). All hydrogen adducts (see Section IV,A) are apparently products of cis addition.

A combination of proton NMR and far-infrared spectroscopy has been used to determine the configurations of adducts formed from the reaction in solution of the planar iridium complex (IV) with a variety of reagents (41).

The stereochemical disposition of methyl-substituted phosphine ligands can be determined by proton NMR spectra (76). Mutually trans phosphines exhibit a P—Me triplet, apparently because of strong coupling between the trans phosphorus nuclei. On the other hand, cis phosphine ligands act as isolated units exhibiting P—Me doublets in the NMR spectrum. With this technique using  $\text{MePPh}_2$  as a ligand, a series of octahedral adducts were prepared from (IV). In all cases the phosphines were shown to remain trans (41).



Jenkins and Shaw (77) have shown that metal-chlorine stretching frequencies in the far-infrared spectra of octahedral complexes are primarily dependent on the nature of the ligand trans to the chlorine. The configurations of a number of adducts derived from (IV) were determined using this technique (41). For example, addition of bromine or iodine to the chloro complex (IV) afforded octahedral complexes (V), apparently by trans addition. Inasmuch as chlorine attacks iridium-bromine or iridium-iodine bonds it was not possible to carry out this reaction by reversing the role of the halogens. It is uncertain whether the configurations of the adducts (V) resulted from thermodynamic or kinetic control.

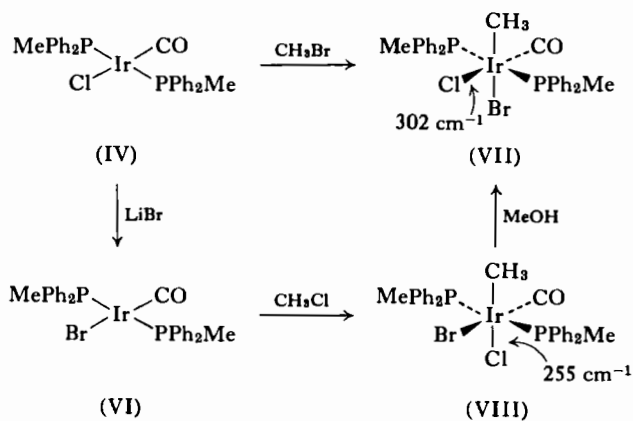
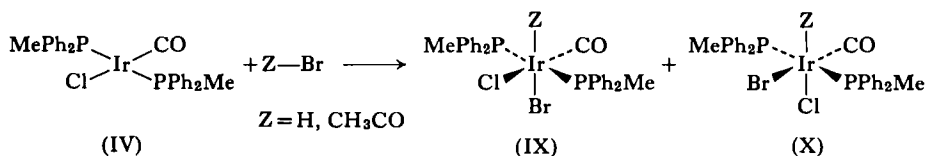


FIG. 3.

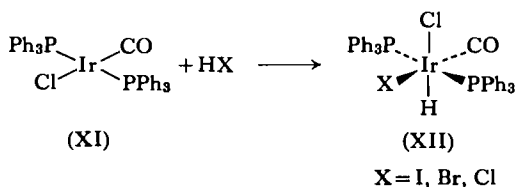
Using the scheme shown in Fig. 3 kinetically controlled trans addition of methyl chloride to the bromo complex (VI) was demonstrated (41). The methyl chloride adduct (VIII) was found to rearrange in a benzene-methanol mixture to the isomer (VII) which was independently prepared by treating the planar chloro complex (IV) with methyl bromide. The iridium-chlorine stretching frequencies shown in Fig. 3 are consistent with model compounds having chlorine trans to methyl or CO. The homogeneity of these isomers was established using thin-layer chromatography. On the basis of independent far-infrared studies, Bennett *et al.* concluded that the added atoms occupy cis positions (11a).

Dry hydrogen bromide and acetyl bromide react with the planar iridium complex (IV) in benzene to form a mixture of two stereoisomers, (IX) and (X) (41). The same mixture of isomers was obtained by adding hydrogen



chloride and acetyl chloride to the planar iridium bromide (VI). The constant isomer ratios from different experiments suggest that the configurations are at equilibrium.

Vaska (120) used far-infrared spectroscopy to study the stereochemistry of the addition of *gaseous* hydrogen halides to the *crystalline* iridium(I) complex (XI). The adducts (XII) are those of cis addition in which the

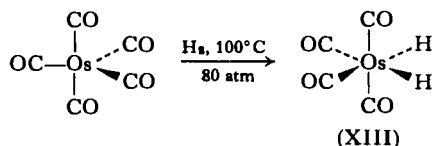


hydride assumes a position trans to chloride. The contrast between the stereochemical course of the homogeneous and heterogeneous addition reactions is remarkable. Reactions of gaseous addenda with solid  $d^8$  substrates have the advantage for stereochemical studies that rearrangements are minimized (120).



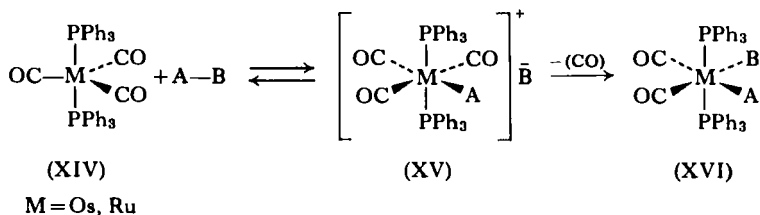
## 2. Additions to Five-Coordinate Complexes

In all cases which have been examined, the final products of the addition of addenda A—B to five-coordinate  $d^8$  complexes are those in which A and B occupy cis positions in an octahedral configuration. Examples include addition of halogens, hydrogen halides and other strong protonic acids, and hydrogen. The reaction of hydrogen with  $\text{Os}(\text{CO})_5$  results in the formation of a cis dihydride (XIII) (83) but it seems likely that this reaction takes place by prior dissociation of a CO group.



With respect to this question it is significant that the corresponding bis phosphine complex *trans*-( $\text{Ph}_3\text{P}$ )<sub>2</sub> $\text{Os}(\text{CO})_3$  is stable to the loss of CO and does not appear to react with hydrogen under moderate conditions (39). The phosphines would be expected to enhance the addition of hydrogen (see Section IV, A) but also to stabilize the osmium–carbonyl bonds through symbiotic bonding effects.

Unlike the above example, the majority of five-coordinate  $d^8$  complexes appear to undergo oxidative-addition reactions in two separate steps. Additions to the bis phosphine complexes of ruthenium(0) (36) and osmium(0) (39) (XIV) are the most thoroughly studied examples of this generalization (see Section IV). The configurations of these complexes have been established by infrared spectroscopy and, in the case of the osmium complex, by X-ray diffraction (72). Addition of an electrophile  $\text{A}^+$  (for example  $\text{H}^+$ ,  $\text{HgX}^+$ , or  $\text{Br}^+$  from  $\text{Br}_2$ ) to the five-coordinate complexes (XIV) results in the formation of an intermediate six-coordinate cation (XV) which can usually be isolated and characterized (see Section IV).



The phosphines are thought to remain *trans* [in a few cases this has been established by NMR using methyl-substituted phosphines (40)]. The final stage of the oxidative addition involves replacement of a CO by the conjugate base  $B^-$ . The *trans* CO groups are mutually labilized by the *trans* effect. Replacement of one of these stereochemically equivalent CO groups by  $B^-$  results in the formation of a *cis* adduct (XVI).

### III

#### INTERMEDIATE EXAMPLES

This section discusses those situations where the addendum does not break into two fragments upon reaction with a  $d^8$  complex. Many of these adducts may be considered either as five-coordinate  $d^8$  complexes or six-coordinate  $d^6$  complexes. Only accurate structural information can decide which description is the more appropriate.

##### A. Oxygen Complexes

Oxygen forms 1:1 adducts with a number of the more reactive unsaturated  $d^8$  complexes (72a, 81, 90, 116); examples are listed in Table I. The best studied system involves reaction of oxygen with  $IrX(CO)(PPh_3)_2$  first reported by Vaska (116). Addition occurs either in solution or by reaction

TABLE I  
ADDITION OF OXYGEN AND SULFUR DIOXIDE TO  $d^8$  COMPLEXES

$d^8$ Substrate <sup>a</sup>	Addendum	Adduct	References
$RhClL_3$	$O_2$	$RhClO_2L_2$	7
$IrX(CO)L_2$ X = Cl, I, $N_3$	$O_2$	$IrX(O_2)(CO)L_2$	35, 72a, 81, 116
$IrCl(CO)L_2L'$	$O_2$	$IrCl(O_2)(CO)L_2L'$	40
$IrCl(CO)L_2$	$SO_2$	$IrCl(SO_2)(CO)L_2$	83a, 121
$[Ir(dppe)_2]Cl$	$O_2$	$[Ir(O_2)(dppe)_2]Cl$	122
$[Ir(dppe)_2]Cl$	$SO_2$	$[Ir(SO_2)(dppe)_2]Cl$	106, 122

<sup>a</sup> L = triphenylphosphine; L' = triphenylarsine; dppe = bis(diphenylphosphino)ethane.

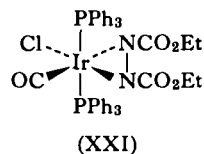
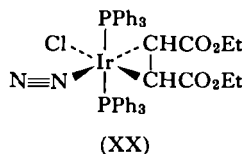
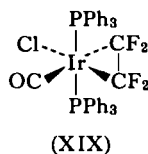
of gaseous oxygen with crystals of the iridium(I) complexes. These reactions are reversible but the iodide complex shows a much greater tendency to



Sulfur dioxide also forms 1 : 1 adducts with four-coordinate  $d^8$  complexes (see Table I) (82, 121, 122). An X-ray diffraction study of the adduct  $\text{IrCl}(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$  revealed a tetragonal pyramidal structure with sulfur dioxide at the apex (83). Sulfur is directly bound to iridium by a long bond (2.49 Å).

### B. Olefin Complexes

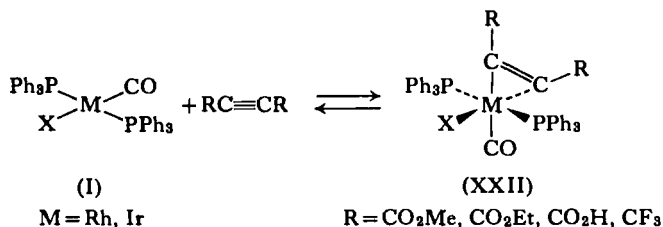
The planar iridium(I) complex (XI) forms 1 : 1 adducts with a number of olefins. Examples include ethylene (125), cyclohexene (31), maleic anhydride (31), tetracyanoethylene (4, 31), and tetrafluoroethylene (100). These complexes reversibly dissociate, their stability being enhanced by electronegative substituents on the olefins. That steric factors play a role in stability of these adducts is illustrated by the failure of  $\alpha$ -methylmaleic anhydride to form a stable adduct (32). Although X-ray diffraction studies have not yet been reported for olefin complexes of this type, the coupling pattern in the  $^{19}\text{F}$  NMR spectra of the tetrafluoroethylene complex suggests that this adduct (XIX) might best be considered an iridium(III) complex with conceptional  $\sigma$ -bonds to the olefin carbons (100). The CO stretching frequency of all such olefin adducts is about  $2030\text{ cm}^{-1}$  (31). Complexes closely related to the olefin adducts are the diethyl maleate complex containing molecular nitrogen (XX) (30), and the complex formed from diethyl azodicarboxylate (XXI) (31). The structures depicted must be considered provisional.



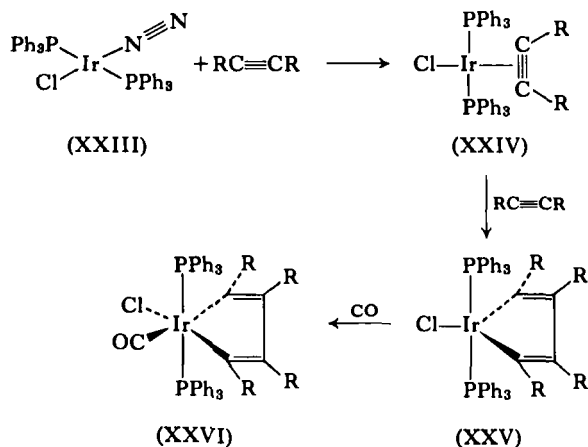
### C. Acetylene Complexes

Acetylenes with electronegative substituents reversibly combine with planar iridium(I) (93, 99) and rhodium(I) complexes (I) to form 1 : 1 adducts (XXII) (31). These are characterized by strong infrared absorption bands in the  $1600\text{--}1800\text{ cm}^{-1}$  region, apparently caused by a stretching mode of the coordinated acetylenic bond. The carbon-carbon bond order in these complexes may approach that of an olefin. In view of a recent

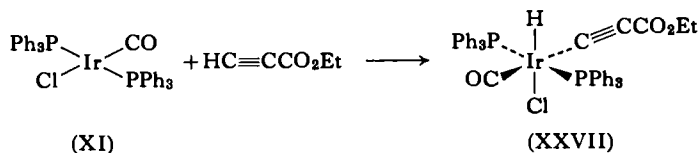
X-ray structural study of a platinum(II)-acetylene complex (63) it seems likely that the acetylenic bond angles in the complexes (XXII) will be found to be closer to  $120^\circ$  than  $180^\circ$ . Both proton NMR and infrared spectra of the complexes (XXII) indicate that the R groups are in different structural environments (31).



A series of novel cyclic compounds has been derived by treating the nitrogen complex (XXIII) (30) with electronegatively substituted acetylenes (31). Initially an acetylene replaces nitrogen to form an iridium(I)-acetylene complex (XXIV) which can be isolated. The coordinated acetylene stretching frequency for such complexes lies in the range  $1780\text{--}1855\text{ cm}^{-1}$ . Addition of another mole of acetylene yields a very stable cyclic complex (XXV) referred to as a "metallocycle" (42). That oxidative addition has taken place is demonstrated by coordination of an additional ligand such as CO or  $\text{ArN}\equiv\text{C}$  with the iridium metallocycle (XXV) ( $\text{R} = \text{CO}_2\text{CH}_3$ ) to form the six-coordinate complexes (XXVI). The coordinatively unsaturated metallocycles (XXV) are active trimerization catalysts for acetylenes.



Acetylenes having a terminal hydrogen sometimes add the acetylenic carbon-hydrogen bond across the planar  $d^8$  complex to form a hexa-coordinate hydridoacetylide complex (31). The only well-studied example is the reaction of ethyl propiolate with the iridium complex (XI) to form (XXVII).



The structure assigned to (XXVII) is primarily based on its infrared spectrum and that of the analogous deuteride. Such hydrido complexes are probably intermediates in the polymerization of terminal acetylenes by transition metal complexes (91). In this regard it is significant that phenylacetylene forms an oligomer in the presence of a catalytic amount of the rhodium complex  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  (32). Rhodium remains chemically bound to this poorly characterized oligomer.

#### IV

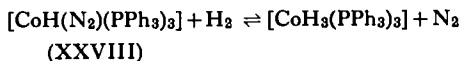
#### EXAMPLES OF OXIDATIVE-ADDITION REACTIONS

In this section additions of various classes of reagents to  $d^8$  complexes are considered.

##### A. Hydrogen

The parallel between hydrogen addition to  $d^8$  complexes and chemisorption on a transition metal surface is striking (124). The ability of the *crystalline* iridium complex (XI) to reversibly add gaseous hydrogen (124) serves to emphasize this analogy.

Only the most reactive  $d^8$  complexes form stable adducts with hydrogen (see Table II). Since these additions are reversible and reasonably rapid it is likely that the failure of other four-coordinate complexes to form stable adducts with hydrogen can be attributed to thermodynamic rather than kinetic control. Although two five-coordinate  $d^8$  complexes,  $\text{Os}(\text{CO})_5$  and  $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ , react with hydrogen (83, 105), it seems probable that the fifth ligand dissociates prior to reaction with hydrogen. The reversible formation of the nitrogen complex (XXVIII) is remarkable (105).



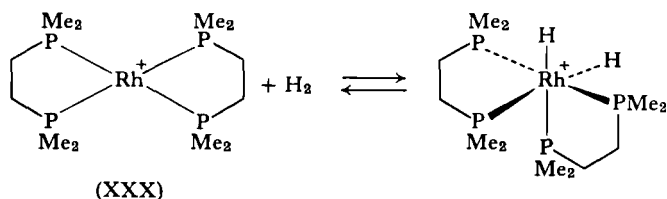
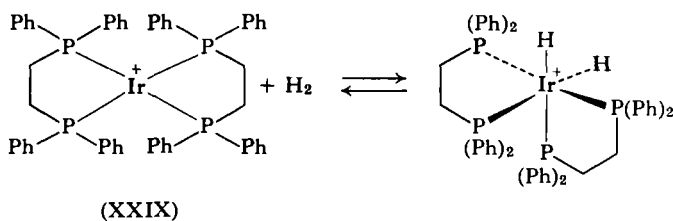
Because of the limited tendency for  $d^8$  complexes to react with hydrogen, this reaction serves as an excellent example of the relative abilities of various metals in Group VIII to undergo oxidative addition and illustrates the influence of ligands on the reactivity of  $d^8$  complexes. For example, the iridium complex  $\text{Ir}^{\text{I}}(\text{CO})(\text{PPh}_3)_2$  readily reacts with hydrogen at atmospheric pressure, but the isostructural rhodium complex does not form a

TABLE II  
ADDITION OF HYDROGEN TO  $d^8$  COMPLEXES

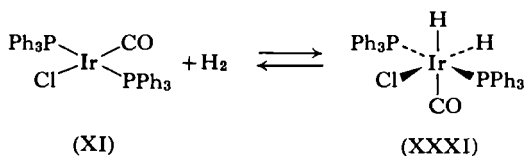
$d^8$ Substrate <sup>a</sup>	$d^8$ Adduct	References
$\text{Os}(\text{CO})_6$	$\text{Os}(\text{H})_2(\text{CO})_4$	83
$[\text{Co}(\text{dppe})_2]\text{Y}$	$[\text{Co}(\text{H})_2(\text{dppe})_2]\text{Y}$	106
$\text{CoH}(\text{N}_2)\text{L}_3$	$\text{Co}(\text{H})_3\text{L}_3$	105
$\text{RhClL}_3$	$\text{RhCl}(\text{H})_2\text{L}_2$	98
$[\text{Rh}(\text{dmpe})_2]\text{Cl}$	$[\text{Rh}(\text{H})_2(\text{dmpe})_2]\text{Cl}$	21
$\text{IrCl}(\text{CO})\text{L}_2$	$\text{IrCl}(\text{H})_2(\text{CO})\text{L}_2$	62, 109, 119, 124, 125
$[\text{Ir}(\text{dppe})_2]\text{X}$	$[\text{Ir}(\text{H})_2(\text{dppe})_2]\text{X}$	106, 122
$\text{IrClL}_3$	$\text{IrCl}(\text{H})_2\text{L}_3$	13, 35
$\text{IrH}(\text{CO})\text{L}_2$	$\text{Ir}(\text{H})_3(\text{CO})\text{L}_2$	86

<sup>a</sup> L = triphenylphosphine; dmpe = bis(dimethylphosphino)ethane; Y =  $\text{ClO}_4$ ,  $\text{BPh}_4$ ; X = Cl, Br, I; dppe = bis(diphenylphosphino)ethane.

stable dihydride. On the other hand, replacing CO by a triphenylphosphine ligand affords a rhodium complex  $\text{RhCl}(\text{PPh}_3)_3$  which readily reacts with hydrogen at atmospheric pressure (98). The rate of hydrogen addition is increased if iodide replaces chloride in the iridium complex (III) (see Section II). Soft  $\sigma$ -donor ligands appear to favor, whereas  $\pi$ -acids seem to reduce, the tendency for a complex to add hydrogen. Further examples of the greater reactivity of iridium compared with rhodium and of the effect of  $\sigma$ -donation in the activation of complexes to add hydrogen are found in the cationic complexes (XXIX) (122) and (XXX) (21). The di[bis(diphenylphosphino)]ethane-iridium complex (XXIX) readily adds hydrogen (at atmospheric pressure) but the analogous rhodium complex does not (21, 106). However, the di[bis(dimethylphosphino)]ethane-rhodium complex (XXX) readily forms a dihydride (21).



The course of hydrogen addition has been found to be *cis* in all cases where the stereochemistry has been examined. The best studied example involves  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ . The NMR spectrum of the dihydride (XXXI) exhibits two proton resonances at 28.4 and 17.3 $\tau$  (62, 109). Each is split into a triplet, indicating the presence of two magnetically equivalent phosphines each *cis* to the hydride. The different structural environment of the hydride groups is consistent with hydride stretching bands at 2222 and 2098  $\text{cm}^{-1}$ . The band at lower frequency is thought to be caused by the hydride which is *trans* to CO. The infrared spectrum of the dideutero complex confirms the assignment of these bands to hydride groups. Strangely, it has been reported that HD is scrambled by addition to the iridium complex (XI), yielding HD,  $\text{D}_2$ , and  $\text{H}_2$  adducts (119).



The practical significance of the hydrogen-addition reaction stems from the fact that this is a key step in the mechanism of catalytic hydrogenation (98). Many of the substrates illustrated in Table II have been found to be homogeneous hydrogenation catalysts (see Section VI). The most effective of these is the catalyst  $\text{RhCl}(\text{PPh}_3)_3$  studied by Wilkinson *et al.* (98).



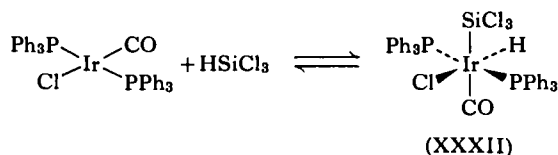
### B. Nonmetal Hydrides

Few reactions of this type have been explored. Thio acids and thiophenols form stable hydrido adducts with the iridium complex (XI) (see Table III).

TABLE III  
ADDITION OF NONMETAL HYDRIDES

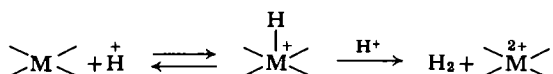
$d^8$ Substrate	Addendum	$d^8$ Adduct	References
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	$\text{HSiCl}_3$	$\text{IrClH}(\text{SiCl}_3)(\text{CO})(\text{PPh}_3)_2$	19
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	$\text{CH}_3\text{C}_6\text{H}_4\text{SH}$	$\text{IrClH}(\text{CH}_3\text{C}_6\text{H}_4\text{S})(\text{CO})(\text{PPh}_3)_2$	40
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	$\text{CH}_3\text{COSH}$	$\text{IrClH}(\text{CH}_3\text{COS})(\text{CO})(\text{PPh}_3)_2$	40

Trichlorosilane reversibly adds the Si—H bond across iridium(I) forming a stable iridium(III) hydride (XXXII) of uncertain stereochemistry (19). Such a complex has been proposed as an intermediate stage in the hydro-silation of olefins catalyzed by  $d^8$  complexes. Undoubtedly many more additions of this type will be examined in the future.



### C. Hydrogen Halides and Other Proton Acids

It is now clear that complexes of transition metals in low oxidation states can act as bases. Proton NMR spectroscopy has been used to survey the protonation of a variety of transition metal complexes (54, 55). The entire idea of oxidative addition is based on the conceptual removal of electrons from such a basic metal center. The relationship between acid-base and oxidation-reduction reactions is particularly evident in cases where a proton becomes attached to a basic metal nucleus causing a two-unit increase in the formal oxidation state of the metal. Once coordinated, the proton is considered a hydride. Indeed the hydrogen often has hydridic character, reacting with another proton to yield hydrogen gas and the metal with an increase of two charge units.



As might be expected four-coordinate  $d^8$  complexes usually react with both the proton and its conjugate anion. However, five-coordinate  $d^8$  complexes may simply react with a proton, forming a cationic complex.

TABLE IV

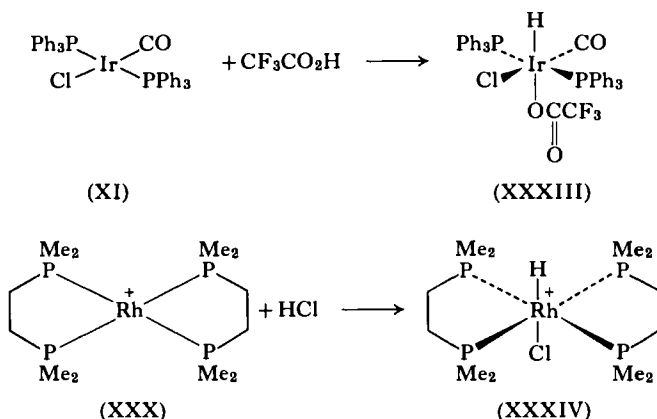
ADDITION OF HYDROGEN HALIDES AND OTHER PROTON ACIDS TO  $d^8$  COMPLEXES

$d^8$ Substrate <sup>a</sup>	Addendum	$d^8$ Adduct	References
Ru(CO) <sub>3</sub> L <sub>2</sub>	HX X = Cl, Br, I, NO <sub>3</sub> , HCO <sub>2</sub> , CF <sub>3</sub> CO <sub>2</sub>	RuX <sub>2</sub> (CO) <sub>2</sub> L <sub>2</sub>	36
Os(CO) <sub>3</sub> L <sub>2</sub>	HX X = Cl, Br, I	OsX <sub>2</sub> (CO) <sub>2</sub> L <sub>2</sub>	39
Os(CO) <sub>3</sub> L <sub>2</sub>	HX X = Cl, Br, BF <sub>4</sub> , PF <sub>6</sub>	[OsH(CO) <sub>3</sub> L <sub>2</sub> ]X	103
[Co(dppe) <sub>2</sub> ]Y Y = ClO <sub>4</sub> , BPh <sub>4</sub>	HX X = Cl, Br, I	[CoXH(dppe) <sub>2</sub> ]Y	106
CoH(dppe) <sub>2</sub>	HClO <sub>4</sub>	[Co(H) <sub>2</sub> (dppe) <sub>2</sub> ]ClO <sub>4</sub>	107
RhClL <sub>3</sub>	HCl	RhCl <sub>2</sub> HL <sub>2</sub>	7
[Rh(dmpe) <sub>2</sub> ]Cl	HX X = Cl, Br	[RhXH(dmpe) <sub>2</sub> ]Cl	21
RhCl(olefin)(CO) <sub>2</sub> olefin = diphenylfulvene	HCl	RhCl <sub>2</sub> H(olefin)(CO) <sub>2</sub>	3
IrX(CO)L <sub>2</sub> X = Cl, Br, I	HY Y = F, Cl, Br, I	IrXYH(CO)L <sub>2</sub>	120, 123
IrX(CO)(PPh <sub>2</sub> Me) <sub>2</sub> X = Cl, Br	HY Y = Cl, Br	IrXYH(CO)(PPh <sub>2</sub> Me) <sub>2</sub>	41
IrCl(CO)L <sub>2</sub>	HX X = HO <sub>2</sub> CCO <sub>2</sub> , CF <sub>3</sub> CO <sub>2</sub>	IrClXH(CO)L <sub>2</sub>	32
IrClL <sub>3</sub>	HCl	IrHCl <sub>2</sub> L <sub>2</sub>	13
[Ir(dppe) <sub>2</sub> ]Cl	HX X = Cl, Br	[IrXH(dppe) <sub>2</sub> ]Cl	122
IrH(CO)L <sub>3</sub>	HX X = Cl, Br	[Ir(H) <sub>2</sub> (CO)L <sub>3</sub> ]X	119
IrH(CO) <sub>2</sub> L <sub>2</sub>	HPF <sub>6</sub>	[Ir(H) <sub>2</sub> (CO) <sub>2</sub> L <sub>2</sub> ]PF <sub>6</sub>	43
PtHCl(PEt <sub>3</sub> ) <sub>2</sub>	HCl	Pt(H) <sub>2</sub> Cl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	26

<sup>a</sup> L = triphenylphosphine; dppe = bis(diphenylphosphino)ethane; dmpe, bis(dimethylphosphino)ethane.

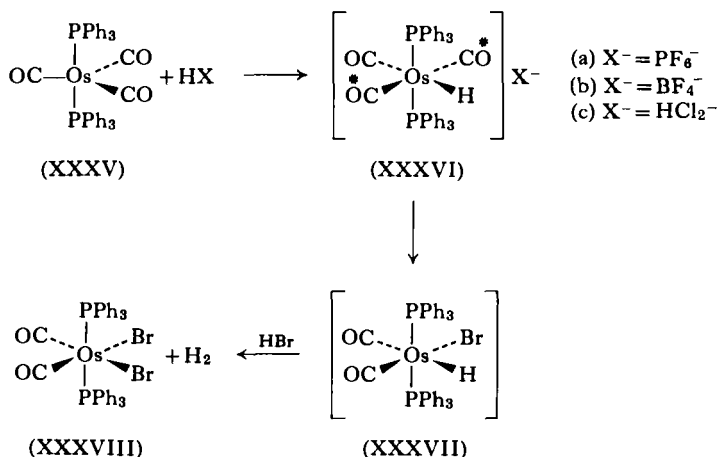
This often results in the labilization of a neutral ligand which is then replaced by the conjugate anion of the acid to yield a neutral complex. Examples of the addition of protonic acids to  $d^8$  complexes are presented in Table IV, but only those instances in which a stable adduct is formed are included.

Four-coordinate complexes of iridium(I) [such as (XI)] reversibly add hydrogen halides (123, 124) and other strong acids (32). The resulting six-coordinate hydrides [such as (XXXIII)] are relatively stable to reaction with an additional proton unless forcing conditions are employed (123). By contrast the isostructural rhodium complex  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  does not form stable adducts with hydrogen halides under moderate conditions. However, ligands with stronger  $\sigma$ -donor properties sufficiently activate rhodium so that stable adducts (XXXIV) are formed even from the cationic complex (XXX) (21). The stereochemistries depicted are not firmly established.



The role of protonic acids in the stepwise oxidative addition of five-coordinate  $d^8$  complexes is well illustrated by reactions of acids with the osmium(0) complex (XXXV). Hexafluorophosphonic and tetrafluoroboric acids form stable adducts (XXXVIa) and (XXXVIb) which have been characterized as 1:1 electrolytes (39, 103). Similar cationic adducts (XXXVIc) have been formed by reaction of  $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$  with dry HCl and HBr gas (103). The osmium(II) hydrido cation (XXXVI) possesses trans CO groups (marked with an asterisk) which are mutually labilized through the trans effect. In the presence of a nucleophilic conjugate anion such as bromide one of these CO groups is replaced to yield a neutral adduct

(XXXVII). This adduct is not isolated but apparently reacts with another mole of HBr, forming  $H_2$  and the final product (XXXVIII). The configurations of the starting  $d^8$  complex (XXXV) and the final product (XXXVIII) are firmly established.



The isostructural ruthenium complex does not stop at an intermediate cationic stage but proceeds to the final neutral product. Many protonic acids have been employed in these oxidations (see Table IV). The proton in such reactions can be replaced by other electrophiles such as  $\text{Br}^+$  or  $\text{HgX}^+$  (see Sections IV, F and D).

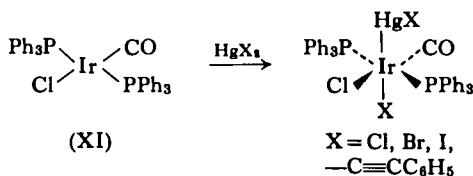
It should be noted that this mechanism explains the acid-catalyzed labilization of  $\text{Fe}(\text{CO})_5$  (9) and the preferential exchange of three CO groups in  $(\text{Ph}_3\text{P})\text{Fe}(\text{CO})_4$  in the presence of strong acids (10). Such iron(0) complexes apparently do not form stable adducts with proton acids but are in equilibrium with small amounts of cationic hydrido complexes.

#### D. Metal Halides

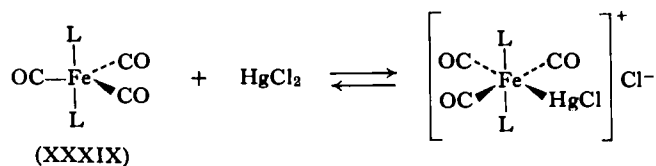
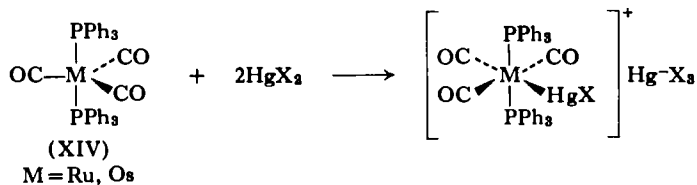
Mercuric halides are Lewis acids and may also be considered pseudohalogens. It is not surprising that mercuric halides readily add to many  $d^8$  complexes (see Table V). Thus the iridium(I) complex (XI) adds mercuric halides, but the isostructural less-reactive rhodium(I) complex does not form a stable adduct (96). Mercuric acetylides also add to the iridium complex (XI) (31).

TABLE V  
ADDITION OF METAL HALIDES TO  $d^8$  COMPLEXES

$d^8$ Substrate	Addendum	$d^6$ Adduct	References
$\text{Fe}(\text{CO})_3\text{L}_2^*$ $\text{L}^* = \text{PPh}_3, \text{P}(\text{OPh})_3$	$\text{HgCl}_2$	$[\text{Fe}(\text{HgCl})(\text{CO})_3\text{L}_2^*]\text{Cl}$	1, 44, 83a
$\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$	$\text{HgX}_2$ $\text{X} = \text{I}, \text{Br}, \text{Cl}$	$[\text{Ru}(\text{HgX})(\text{CO})_3(\text{PPh}_3)_2]\text{HgX}_3$	37
$\text{Os}(\text{CO})_3(\text{PPh}_3)_2$	$\text{HgX}_2$ $\text{X} = \text{I}, \text{Br}, \text{Cl}$	$[\text{Os}(\text{HgX})(\text{CO})_2(\text{PPh}_3)_2]\text{HgX}_3$	37
$\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$	$\text{HgCl}_2$	$[\pi\text{-C}_5\text{H}_5\text{Co}(\text{HgCl})(\text{CO})_2]\text{Cl}$	2, 44
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	$\text{HgX}_2$ $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN},$ $\text{SCN}, \text{OAc}$	$\text{IrClX}(\text{HgX})(\text{CO})(\text{PPh}_3)_2$	96
$\text{IrCl}(\text{CO})(\text{PPh}_2\text{Me})_2$	$\text{HgCl}_2$	$\text{IrCl}_2(\text{HgCl})(\text{CO})(\text{PPh}_2\text{Me})_2$	41
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	$\text{SnCl}_4$	$\text{IrCl}_2(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2$	109



The addition of mercuric halides to five-coordinate  $d^8$  complexes usually stops at an intermediate stage where  $\text{HgX}^+$  has formed a bond with the central metal to afford a cationic  $d^6$  complex. Reactions of the ruthenium(0) and osmium(0) complexes (XIV) with mercuric halides illustrate this type of behavior (37). Such reactions do not always go to completion. For



example the iron(0) complexes (XXXIX) are in equilibrium with mercuric chlorides (1, 44). The equilibrium lies to the right where  $L = P(OPh)_3$ , but at an intermediate stage where  $L = P(Ph)_3$ .

Tin tetrachloride forms a stable adduct with the iridium complex (XI) (109) (see Table V). The scope of such metal halide additions is not yet clear.

### E. Alkyl and Acyl Halides

Both four- and five-coordinate  $d^8$  complexes react with alkyl halides and acyl halides (see Tables VI and VII). Only the most reactive alkylating agents and  $d^8$  complexes have been found to form stable adducts. Few

TABLE VI  
ADDITION OF ALKYL HALIDES TO  $d^8$  COMPLEXES

$d^8$ Substrate <sup>a</sup>	Addendum	$d^8$ Adduct	References
$Fe(CO)_5$	$CH_2=C(CH_3)CH_2I$	$\pi-(C_4H_7)FeI(CO)_3$	101
$Ru(CO)_3L_2$	$CH_3I$	$RuICH_3(CO)_2L_2$	40
$\pi-C_5H_5Co(CO)_2$	$CH_2=CHCH_2X$ X = Cl, Br, I	$\pi-C_5H_5CoX(\pi-C_3H_5)$ and $[\pi-C_5H_5Co(CO)(\pi-C_3H_5)]PF_6$	66 58
$RhCl(olefin)(CO)_2$ olefin = diphenyl- fulvene	$CH_3I$	$RhClI(CH_3)(olefin)(CO)_2$	3
$RhCl(CO)(PR_3)_2$ R = $C_2H_5$ , $n-C_4H_9$	$CH_3I$	$RhClI(CH_3)(CO)(PR_3)_2$	67
$RhClL_3$	$CH_3I$	$RhClI(CH_3)(ICH_3)L_2$	82a
$RhClL_3$	$CH_2=CR-CH_2Cl$ R = H, $CH_3$	$RhCl_2(C_3H_4R)L_2^b$	82a
$RhCl(AsPh_3)_3$	$CH_2=C(CH_3)CH_2Cl$	$RhCl_2(\pi-C_4H_7)(AsPh_3)_2$	82a
$IrCl(CO)L_2$	RI R = $CH_3$ , $CH_2=CH-CH_2$ ,	$IrClI(R)(CO)(L_2)$	66
$IrBr(CO)(PEt_2Ph)_2$	$CH_3Br$	$IrBr_2(CH_3)(CO)(PEt_2Ph)_2$	23
$IrX(CO)(PEt_2Ph)_2$	$CH_2=CHCH_2X$ X = Br, Cl	$IrX_2(\sigma-C_3H_5)(CO)(PEt_2Ph)_2$	23
$IrX(CO)(PPh_2Me)_2$	$CH_3Y$ X = Y = Cl, Br X = Cl, Y = Br, I X = Br, Y = Cl	$IrXY(CH_3)(CO)(PPh_2Me)_2$	41
$PtI(CH_3)(PEt_3)_2$	$CH_3I$	$PtI_2(CH_3)_2(PEt_3)_2$	24

<sup>a</sup> L = triphenylphosphine.

<sup>b</sup> Both  $\sigma$ - and  $\pi$ -allyl complexes are formed.

TABLE VII  
 ADDITION OF ACYL HALIDES TO  $d^8$  COMPLEXES

$d^8$ Substrate <sup>a</sup>	Addendum	$d^6$ Adduct	References
$\text{IrX}(\text{CO})(\text{PPh}_2\text{Me})_2$	$\text{CH}_3\text{COY}$	$\text{IrXY}(\text{CH}_3\text{CO})(\text{PPh}_2\text{Me})_2$ $\text{X}=\text{Y}=\text{Cl}, \text{Br}$ $\text{X}=\text{Cl}, \text{Y}=\text{Br}$ $\text{X}=\text{Br}, \text{Y}=\text{Cl}$	41
$\text{IrX}(\text{CO})(\text{PEt}_2\text{Ph})_2$	$\text{RCOX}$	$\text{IrX}_2(\text{RCO})(\text{CO})(\text{PEt}_2\text{Ph})_2$ $\text{X}=\text{Cl}; \text{R}=\textit{n}\text{-Pr}, \textit{iso}\text{-Pr}, \text{Et},$ $\text{Me}, \text{Am}, \text{PhCH}=\text{CH}$ $\text{X}=\text{Br}, \text{R}=\text{Me}$	23
$\text{IrBr}(\text{CO})\text{L}_2$	$\text{CH}_3\text{COBr}$	$\text{IrBr}_2(\text{CH}_3\text{CO})(\text{CO})\text{L}_2$	23

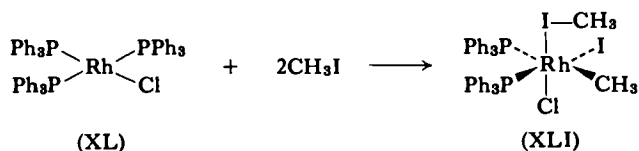
<sup>a</sup>  $\text{L} = \text{PEt}_3, \text{PEt}_2\text{Ph}, \text{AsEt}_2\text{Ph}.$

five-coordinate complexes have been alkylated, but it seems likely that purposeful efforts to explore the scope of this reaction have not been made.

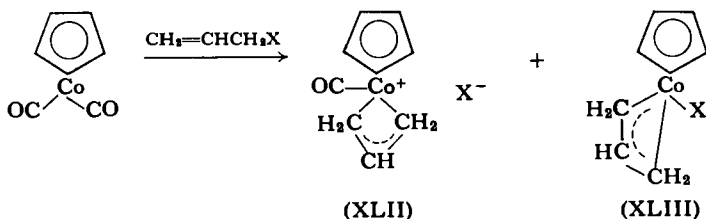
Studies of four-coordinate  $d^8$  complexes clearly indicate that the ligands have a pronounced effect on the tendency of the complex to undergo alkylation. Complexes of alkylphosphines are more reactive than those of arylphosphines. The stronger  $\pi$ -acid CO is deactivating compared with triphenylphosphine. Iridium complexes form much more stable adducts than analogous rhodium complexes. The latter fail to react unless activating ligands are present. Kinetic evidence (presented in Section II,B) suggests a highly polar activated complex and that these reactions are best considered as  $\text{S}_{\text{N}}2$  displacements on carbon by the nucleophilic transition metal (28). The effect of the ligands is readily interpreted on this basis. Ligands which build up negative charge on the central metal make the metal a more effective nucleophile. These alkylations are usually reversible.

The influence which the other ligands have on the alkylation of  $d^8$  complexes is illustrated by the addition of methyl iodide to the tris(phosphine)-rhodium complex (XL) (82a) but not to the similar complex  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  in which a CO group has replaced a phosphine. However, the analogous iridium complex  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  reacts with methyl iodide (see Section II,B) (23, 41, 67). The rhodium adduct (XLI) is novel inasmuch as it contains two molecules of methyl iodide, the second apparently being bound through iodine (82a). The detailed stereochemistry

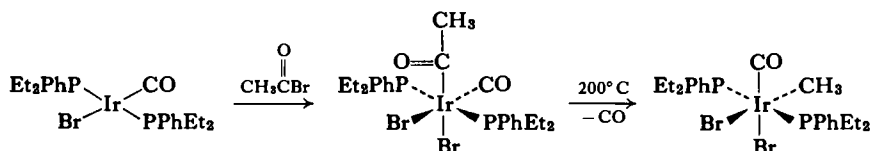
of (XLI) is unknown, but it is thought that the phosphines remain *cis*. More recently the iridium analogue of (XLI) has been prepared (12).



Allyl halides add to the more reactive  $d^8$  complexes. Both  $\sigma$ - and  $\pi$ -allyl complexes are found, occasionally both in the same system. An example of this reaction with allyl chloride is that of  $\pi$ -cyclopentadienylcobalt dicarbonyl discovered by Fischer (58) and reinvestigated by Heck (66). Both cationic (XLII) and neutral complexes (XLIII) are formed, depending on the conditions. The cationic  $\pi$ -allyl complex (XLII) is interesting in that this is another example of the stepwise addition of an electrophile to a five-coordinate  $d^8$  complex. The reader should remember that the formation of the  $\pi$ -allyl group entails the loss of an additional neutral ligand.



Acyl halides also add to  $d^8$  complexes but few examples have been reported. The resulting acyl complexes are sometimes quite stable, although at higher temperatures these can be decarbonylated (23).



## F. Halogens

With the exception of nickel(II) and palladium(II) complexes, all of the  $d^8$  complexes of Group VIII metals form stable adducts with halogens.



Examples are gathered in Table VIII, but this is by no means an exhaustive list.

TABLE VIII  
ADDITION OF HALOGENS TO  $d^8$  COMPLEXES

$d^8$ Substrate <sup>a</sup>	Addendum <sup>b</sup>	$d^6$ Adduct	References
Fe(CO) <sub>5</sub>	X <sub>2</sub>	<i>cis</i> -FeX <sub>2</sub> (CO) <sub>4</sub>	71
Fe(dmpe) <sub>2</sub>	I <sub>2</sub>	FeI <sub>2</sub> (dmpe) <sub>2</sub>	27
Fe(CO) <sub>3</sub> L <sub>2</sub>	X <sub>2</sub>	FeX <sub>2</sub> (CO) <sub>3</sub> L	70
Fe(PF <sub>3</sub> ) <sub>5</sub>	X <sub>2</sub>	FeX <sub>2</sub> (PF <sub>3</sub> ) <sub>4</sub>	80
Ru(CO) <sub>3</sub> L <sub>2</sub> <sup>*</sup> L <sup>*</sup> = PPh <sub>3</sub> , PPh <sub>2</sub> Me	X <sub>2</sub>	RuX <sub>2</sub> (CO) <sub>3</sub> L <sub>2</sub> <sup>*</sup>	36
Os(CO) <sub>3</sub> L <sub>2</sub>	X <sub>2</sub>	[OsX(CO) <sub>3</sub> (L <sub>2</sub> )]X	39, 103
$\pi$ -C <sub>5</sub> H <sub>5</sub> M(CO) <sub>2</sub> M = Co, Rh	I <sub>2</sub>	$\pi$ -C <sub>5</sub> H <sub>5</sub> MI <sub>2</sub> (CO)	69, 78
RhCl(CO)L <sub>2</sub> <sup>*</sup> L <sup>*</sup> = PPh <sub>3</sub> , AsPh <sub>3</sub> , SbPh <sub>3</sub> , PPh <sub>2</sub> Me	X <sub>2</sub>	RhClX <sub>2</sub> (CO)L <sub>2</sub> <sup>*</sup>	114
[Rh(dmpe) <sub>2</sub> ]Cl	Z <sub>2</sub> Z = Cl, Br	[RhZ <sub>2</sub> (dmpe) <sub>2</sub> ]Cl	21
[IrY(CO)L <sub>2</sub> <sup>*</sup> ] L <sup>*</sup> = PPh <sub>3</sub> , PPh <sub>2</sub> Me Y = Cl	X <sub>2</sub>	IrYX <sub>2</sub> (CO)L <sub>2</sub> <sup>*</sup>	41, 124
[Ir(SnCl <sub>3</sub> )QAS]	Cl <sub>2</sub>	[IrCl(SnCl <sub>3</sub> )QAS]Cl	102
[Pt(en) <sub>2</sub> ]Cl <sub>2</sub>	Cl <sub>2</sub>	<i>trans</i> -[PtCl <sub>2</sub> (en) <sub>2</sub> ]Cl <sub>2</sub>	8
[PtY <sub>2</sub> L <sub>2</sub> <sup>*</sup> ] Y = Cl, I, Me L <sup>*</sup> = PEt <sub>3</sub> , AsEt <sub>3</sub>	X <sub>2</sub> <sup>c</sup>	PtY <sub>2</sub> X <sub>2</sub> L <sub>2</sub> <sup>*</sup>	20, 24, 94

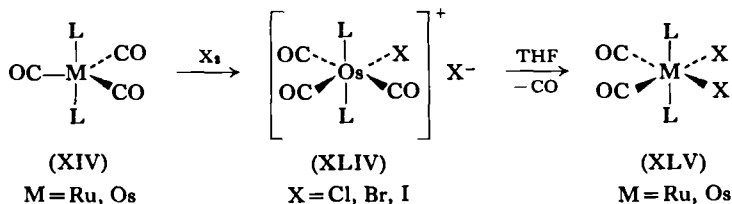
<sup>a</sup> dmpe = bis(dimethylphosphino)ethane; QAS = tris(*o*-diphenylarsinophenyl)-arsine; L = triphenylphosphine.

<sup>b</sup> X = Cl, Br, I.

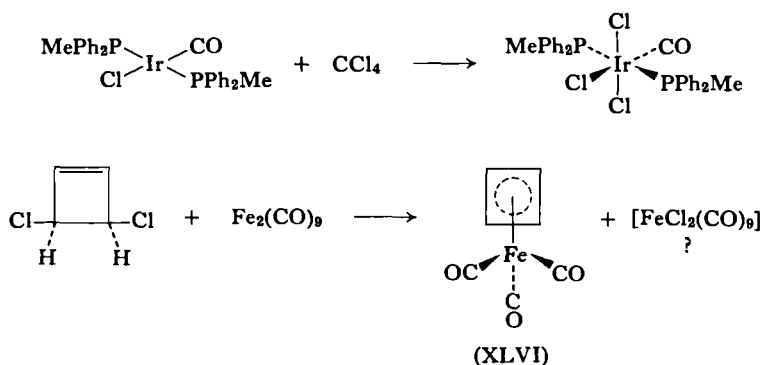
<sup>c</sup> For Y = Me, X = I only.

Five-coordinate  $d^8$  complexes add halogens under very mild conditions, usually with loss of a neutral ligand to form *cis* dihalo compounds. Comparison with the analogous ruthenium(0) and osmium(0) compounds (XIV) reveals the stepwise nature of halogenation. In the case of the osmium complex a cationic intermediate (XLIV), which has been isolated and characterized, is formed (39). Warming this cationic complex in tetrahydrofuran results in the loss of a mole of CO and the formation of the *cis* dihalide (XLV). The intermediate ruthenium complex is apparently too

labile to be isolated so that only the final product is obtained (36). Apparently the mutually trans CO groups labilize one another so that one is easily replaced by halide.



Addition of halogens to planar  $d^8$  complexes is straightforward and does not deserve further comment. However, it should be noted that halogenation can also be achieved by treatment with the carbon tetrahalides (26, 41, 67). The mechanism of this reaction is obscure but a radical path may be involved (104). The fate of the carbon fragment has not been determined but it may be anticipated that carbene like intermediates could be formed in this way. A related process is the halogenation of reactive four-coordinate  $d^8$  complexes by vicinal dihalides which are converted into olefins. Only two examples have been described (28, 56a). The more interesting involves the formation of the cyclobutadiene complex (XLVI) (56a).



### G. Pseudohalogens

Few types of pseudohalogens have been treated with  $d^8$  complexes (for examples see Table IX) and this is a promising area for further work.

Perfluoroalkyl iodides can be considered as pseudohalogens and it is not surprising that these add to  $d^8$  complexes under mild conditions. Both

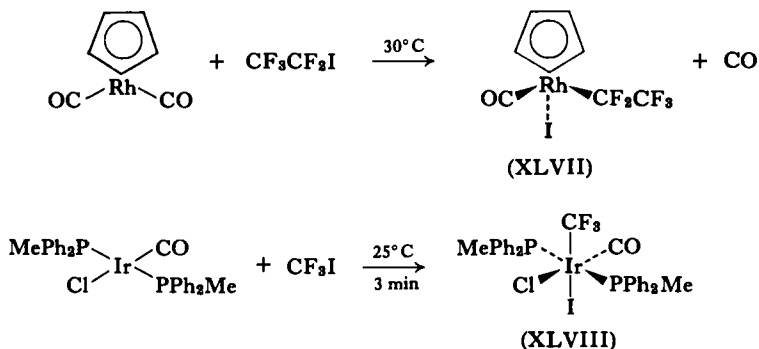
TABLE IX  
ADDITION OF PSEUDOHALIDES TO  $d^8$  COMPLEXES

$d^8$ Substrate	Addendum	$d^6$ Adduct	References
$\text{Fe}(\text{CO})_5$	$\text{C}_3\text{F}_7\text{I}$	$\text{C}_3\text{F}_7\text{FeI}(\text{CO})_4$	79a, 88
$\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$	$\text{R}_\text{F}\text{I}^a$	$\pi\text{-C}_5\text{H}_5\text{CoIR}_\text{F}(\text{CO})$	79, 89
$\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})(\text{PPh}_3)$	$\text{R}_\text{F}\text{I}$	$\pi\text{-C}_5\text{H}_5\text{CoIR}_\text{F}(\text{PPh}_3)$	78
$\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})_2$	$\text{R}_\text{F}\text{I}$	$\pi\text{-C}_5\text{H}_5\text{RhIR}_\text{F}(\text{CO})$	89
$\text{IrCl}(\text{CO})\text{L}_2^b$	$\text{R}_\text{F}\text{I}$	$\text{IrClIR}_\text{F}\text{COL}_2$	41
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	$\text{RSO}_2\text{Cl}$	$\text{IrCl}_2(\text{RSO}_2)(\text{CO})(\text{PPh}_3)_2$	38
	R = Me, Et, $n$ -Pr, $p$ -MeC <sub>6</sub> H <sub>4</sub> , $p$ -ClC <sub>6</sub> H <sub>4</sub> , $p$ -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SCl	$\text{IrCl}_2((\text{NO}_2)_2\text{C}_6\text{H}_3\text{S})(\text{CO})(\text{PPh}_3)_2$	40

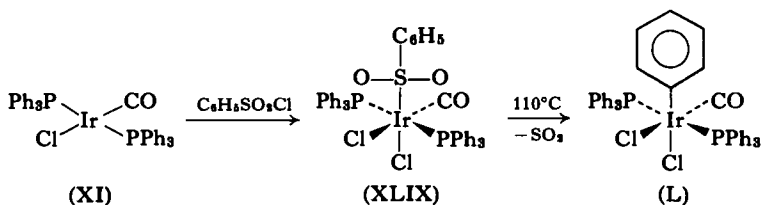
<sup>a</sup>  $\text{R}_\text{F} = \text{CF}_3, \text{C}_2\text{F}_5, n\text{-C}_3\text{F}_7$ .

<sup>b</sup>  $\text{L} = \text{PPh}_3, \text{PPh}_2\text{Me}$ .

four- and five-coordinate  $d^8$  complexes react with these reagents. It is surprising that  $\text{Fe}(\text{CO})_5$  reacts with perfluoropropyl iodide (88) whereas  $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$  does not (40). The rhodium(III) adduct (XLVII) is dissymmetric, as revealed by the AB coupling pattern of the  $\alpha\text{-CF}_2$  group in the  $^{19}\text{F}$  NMR spectrum (89). The detailed configuration of the iridium(III) adduct (XLVIII) is uncertain, but it is known to consist of a single stereoisomer (41).



Both aromatic and aliphatic sulfonyl halides react with the iridium(I) complex (XI) to form octahedral S-bonded sulfinate derivatives such as (XLIX) (38). These are characterized by intense infrared stretching frequencies centered near 1235 and 1065  $\text{cm}^{-1}$ , reminiscent of sulfones. The low frequencies of these absorptions suggest that the S-bonded sulfinate group is a strong  $\pi$ -acid. Certain of the aromatic sulfonates eliminate  $\text{SO}_2$  upon heating, yielding iridium(III) aryls such as (L) (38). The scope of this gas-forming elimination reaction is uncertain.

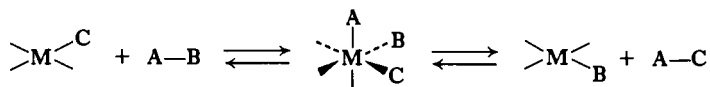


## V

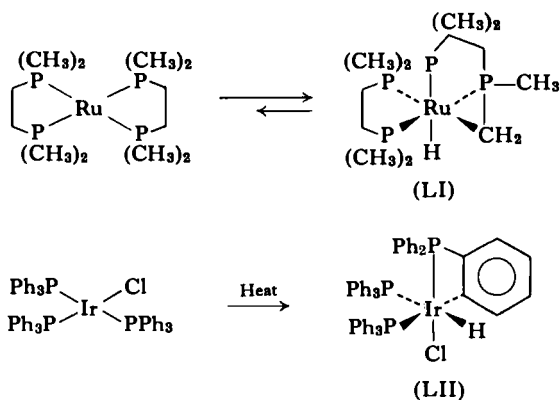
### ADDITION-ELIMINATION REACTIONS

Oxidative-addition reactions are often reversible. There are a number of transformations involving  $d^8$  complexes which can be interpreted by

oxidative addition followed by a reductive elimination. In several examples this provides a mechanism for the interchange of groups of the addendum and the  $d^8$  complex. Such reactions seem limited to the unsaturated  $d^8$  complexes.

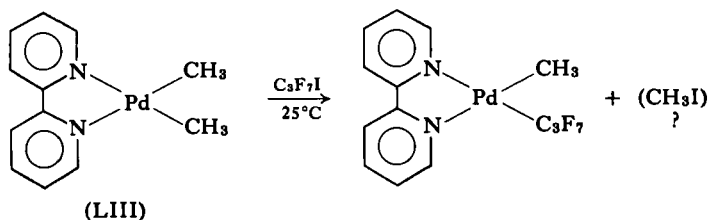


Perhaps the most remarkable addition-elimination reactions are tautomeric transformations whereby a four-coordinate  $d^8$  complex becomes six-coordinate by insertion of the metal into a carbon-hydrogen bond on one of the ligands, forming an octahedral complex with new metal-carbon

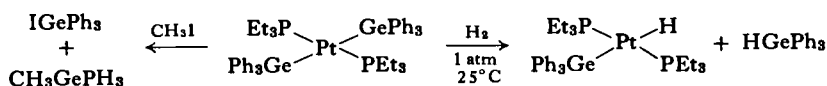


and metal-hydrogen  $\sigma$ -bonds (12). Only the most reactive  $d^8$  complexes exhibit this behavior. Examples are the formation of the ruthenium and iridium adducts (LI) and (LII). The first reaction is reversible (22) but the second apparently is not (12).

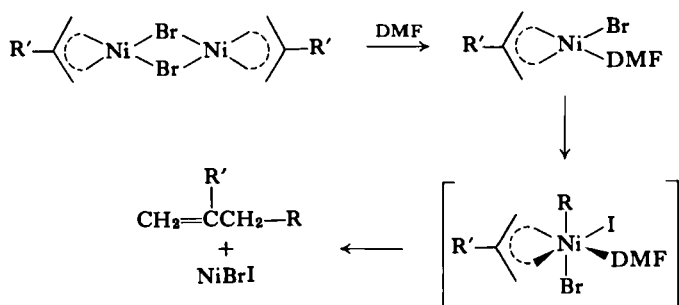
The stepwise replacement of methyl groups in the palladium(II) complex (LIII) by perfluoropropyl groups through reaction with perfluoropropyl iodide may go through an octahedral palladium(IV) intermediate (85). The strong  $\sigma$ -donor character of methyl groups may provide activation for the palladium reaction. A related cleavage of platinum methyl groups through iodination has been shown (24) to involve prior oxidative addition. Cleavage of platinum-carbon bonds by protonic acids may also take place in this way (11).



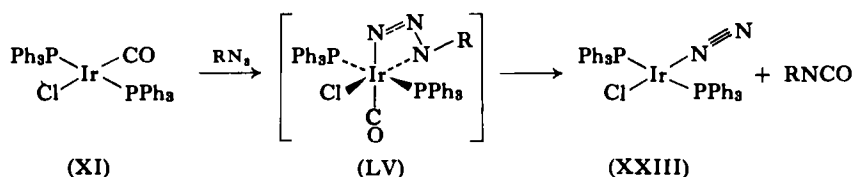
The facile hydrogenolysis of platinum(II)-aryl and platinum(II)-chloride bonds (the latter by reaction with silicon-hydride bonds as well as hydrogen) probably involves oxidative addition followed by reductive elimination (24, 25). It has been suggested that the ready hydrogenolysis of platinum-germanium bonds goes through such a mechanism. Related cleavages of platinum-germanium bonds through reactions with methyl iodide and hydrogen chloride also probably take place in this manner (53).



Corey *et al.* (45-47) have described a remarkable coupling reaction involving  $\pi$ -allylnickel(II) bromide dimers (LIV) and alkyl or aryl iodides. The mechanism proposed for this reaction is an example of oxidative addition followed by reductive elimination. Apparently the  $\pi$ -allyl group activates nickel to oxidative addition by increasing the charge on nickel. The reaction is very sensitive to the nature of the solvent. Dimethylformamide (DMF) was found to be a very effective solvent. It was suggested that the solvent plays a role by acting as a weakly held ligand. Below is a modification of Corey's mechanism (46).



The reaction of organic azides with the iridium(I) carbonyl (XI) to form the nitrogen complex (XXIII) can be interpreted in terms of oxidative addition to form the intermediate (LV) which collapses to the product (XXIII) and an organic isocyanate (34). It is curious that the isocyanate returns to react with the nitrogen complex (XXIII) unless the isocyanate is intercepted by an alcohol. The rate of formation of the nitrogen complex (XXIII) follows the equation:  $\text{rate} = k_2[\text{IrCl}(\text{CO})(\text{PPh}_3)_2][\text{RN}_3]$  (35). The azide must function as an electrophile since acid azides react about 20 times faster than phenyl azide. The postulated intermediate (LV) was not detected kinetically.



It is interesting that this scheme can serve as a pathway to catalyze the reaction between organic azides and CO (33). Carbon monoxide reacts with (XXIII), displacing nitrogen and forming (XI). Diazomethane, which is electronically similar to an organic azide, also reacts with (XI). However, in this instance nitrogen is expelled and a complex of uncertain structure which retains the methylene fragment is formed (87).

Other apparent examples of addition-elimination reactions are to be found in reactions catalyzed by  $d^8$  complexes (see Section VI).

## VI

### EXAMPLES IN HOMOGENEOUS CATALYSIS

Many of the recently discovered homogeneous catalysts are  $d^8$  complexes. Oxidative-addition and reductive-elimination reactions are usually key steps in the mechanisms by which these catalysts function. In a few instances the mechanisms of these catalytic reactions have been elucidated. Selected examples are presented in this section.

#### A. Hydrogenation

A substantial percentage of the transition metal complexes which catalyze the hydrogenation of olefins and acetylenes have a  $d^8$  configuration.

Examples include  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  (125),  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$  (117),  $\text{RhCl}(\text{PPh}_3)_3$  (98),  $\text{Fe}(\text{CO})_5$  (59, 60), and platinum(II) complexes containing  $\text{SnCl}$  ligands (5, 6, 51, 73, 75, 108). The catalyst,  $\text{RhCl}(\text{PPh}_3)_3$ , is the most useful, and the mechanism by which it functions is the most thoroughly understood (98). This section will be restricted to a discussion of this catalyst.

A homogeneous hydrogenation catalyst must carry out three basic reactions: hydrogen activation through the formation of transition metal hydrides, olefin activation through the formation of  $\pi$ -complexes, and hydrogen transfer. For a catalyst to be effective these three stages must be properly synchronized. It should be mentioned that some  $d^8$  complexes catalyze the hydrosilation of olefins. It has been proposed that hydrosilation and hydrogenation take place via similar mechanisms with the  $\text{Si-H}$  bond taking the part of the  $\text{H-H}$  bond (19).

The  $(\text{Ph}_3\text{P})_3\text{RhCl}$  catalyst efficiently catalyzes the hydrogenation of relatively unhindered olefins and acetylenes at ambient temperatures and subatmospheric pressures. Olefin isomerization does not accompany reduction. Hydrogen enters *cis* from the least-hindered face of the olefin (14, 56). Isotopic hydrogen scrambling is minimal compared with heterogeneous catalysts (14, 56) but under certain conditions scrambling will occur (97, 98). Organic compounds containing sulfur have been hydrogenated using this catalyst (15). The stereospecificity and selectivity of this reaction have been applied to natural product chemistry (14, 15, 18, 56).

The mechanism (Fig. 4) by which  $\text{RhCl}(\text{PPh}_3)_3$  catalyzes the hydrogenation of olefins was elucidated by Wilkinson and co-workers (98). This scheme is based on kinetic studies and independent evidence for several of the steps. In solution one phosphine ligand dissociates from the starting complex and is thought to be replaced by a solvent molecule. The labile coordination site may be occupied by an olefin but this step is nonproductive in the hydrogenation reaction. Olefin complexes such as (LVII) have been characterized. Ethylene, which forms a very stable complex ( $k_2$  large), is not hydrogenated by this catalyst. The solvent complex (LVI) undergoes oxidative addition through reaction with hydrogen to form the *cis* dihydride (LVIII). Replacement of coordinated solvent by an olefin leads to the intermediate or activated complex (LIX) containing two hydrides and the olefin in adjacent positions on a single face of the octahedron. The stereospecificity of the reduction has been explained by the geometry of (LIX) and the simultaneous transfer of two hydrogen atoms to the olefin.



Recent studies have shown that transfer of the two hydrogens can be stepwise (13b).

That the olefin must be coordinated is suggested by the slower reduction of more hindered olefins and the poisoning of the catalyst with competing ligands such as acetonitrile, pyridine, or carbon monoxide (98). The planar olefin complexes (LVII) are apparently not capable of adding hydrogen. The  $\pi$ -acid character of the olefin tips the sensitive balance of this oxidative-addition reaction (see Section IV,A). Even though the ethylene complex does not react with hydrogen, stoichiometric reduction takes place when the dihydride (LVIII) is treated with ethylene.

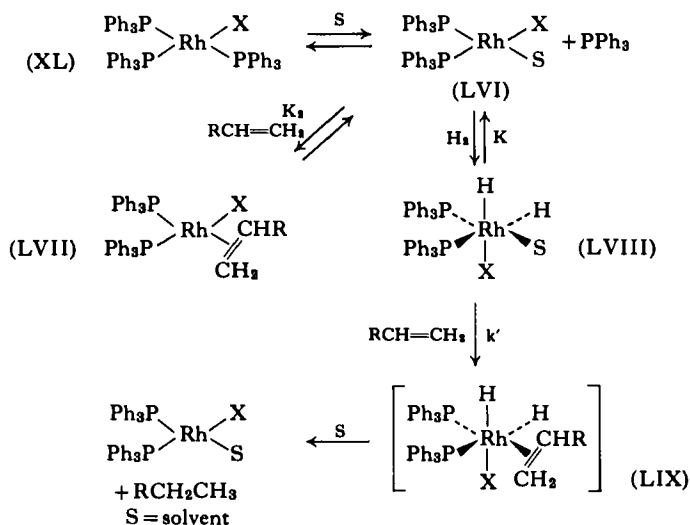


FIG. 4.

The nature of the halide affects the overall rate of the reaction ( $\text{I} > \text{Br} > \text{Cl}$ ). This result is partially accounted for by the trend in  $K_2$  ( $\text{Cl} > \text{Br} > \text{I}$ ). The overall catalytic reaction depends on a delicate balance of the two equilibria  $K_1$  and  $K_2$  and the rate  $k'$ .

Many of the other  $d^8$  hydrogenation catalysts differ from  $(\text{Ph}_3\text{P})_3\text{RhCl}$  inasmuch as the former have at least one stage involving a single transition metal-hydride bond. Such catalysts usually cause olefin isomerization (49, 52) and isotopic hydrogen exchange (between  $\text{H}_2$ , the substrate, and protic solvents). Hydrogen activation can also take place through protonation of the transition metal. This provides a basis for activation of such catalysts by acids (115, 115a).

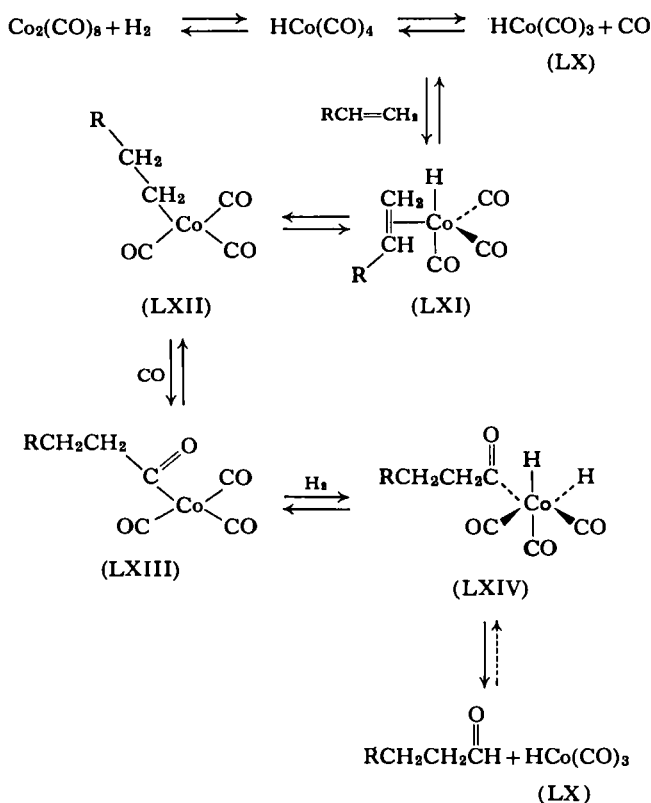


FIG. 5.

### B. Hydroformylation

Heck has formulated a mechanism which accounts for hydroformylation of olefins catalyzed by cobalt carbonyl (68). A *modification* of this mechanism is presented in Fig. 5. Cobalt octacarbonyl reacts with hydrogen to form the tetracarbonyl hydride. It is proposed that this coordinatively saturated complex loses a CO group to form the four-coordinate hydride (LX). Coordination of an olefin yields the olefin complex (LXI). Migration of hydride yields an unsaturated alkyl complex (LXII). Further insertion of a CO group (undoubtedly by a migration mechanism) affords the four-coordinate acyl cobalt(I) complex (LXIII). Oxidative addition of hydrogen affords the hypothetical dihydride (LXIV), which eliminates the product aldehyde and regenerates the cobalt(I) hydride catalyst (LX). This latter

process is reductive elimination. Olefin isomerization, isomer ratios, isotopic hydrogen scrambling, and the rate dependence on CO concentration can be rationalized by this scheme. This mechanism is controversial; however, each stage has a reasonable analogy in the chemistry of well-characterized organometallic complexes. Alkyl migration to an adjacent (cis) carbon monoxide has been demonstrated in the case of  $\text{CH}_3\text{Mn}(\text{CO})_5$  (91a).

Other  $d^8$  complexes are effective hydroformylation catalysts. Examples include  $\text{RhCl}(\text{PPh}_3)_3$  (74),  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  (64), and  $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$  (57).

### C. Decarbonylation

The complex (XL) has also been found to catalyze the decarbonylation of acid halides (17, 111, 112). Aryl halides yield aryl halides whereas acyl halides having a  $\beta$ -hydrogen give rise to olefins (111, 112). These reactions are usually carried out at the boiling point of the acid chloride. Blum *et al.* (17) have proposed a mechanism for the reaction with aryl halides (Fig. 6). The proposed scheme is based on product yields and infrared spectra of certain isolated intermediates.

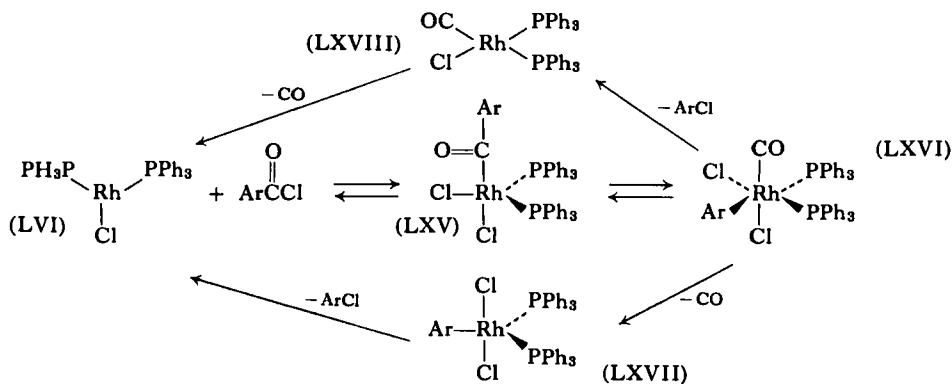
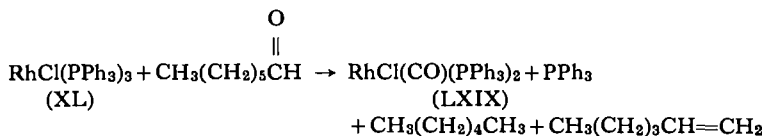


FIG. 6.

The initial step is oxidative addition of the acid chloride to the dissociated form of the complex (LVI) to form the acyl complex (LXV). Aryl migration (reverse insertion) affords a supposed intermediate (LXVI) which can eliminate CO to form (LXVII), which in turn loses aryl halide to regenerate the catalyst. Alternatively (LXVI) can lose aryl halide (reductive elimination) to form a rhodium carbonyl (LXVIII). It is thought that this path is

deactivating and that (LXVIII) must lose a carbonyl group before catalytic activity can be regained. It is interesting that benzyl chlorides can be carbonylated in the presence of this catalyst (111). This is suggested by the reversal of several of these steps. The reductive elimination of an aryl halide should be irreversible but the reverse of this reaction is well known for alkyl halides (see Section IV,E). Aryl sulfonyl halides can be converted to aryl halides by this versatile catalyst (16).

Aldehydes are stoichiometrically decarbonylated by reaction with (XL) under mild conditions (17, 98, 110, 113). Aromatic aldehydes yield aromatic hydrocarbons whereas aliphatic aldehydes form saturated hydrocarbons and olefins. The latter minor products can be considered to arise from a reverse hydroformylation reaction. The initial step of this reaction is probably the oxidative addition of an aldehyde C—H bond to the rhodium(I) complex. However, a stable adduct of this type has not yet been reported. The driving force in these reactions is derived from the stability of the carbonyl (LXIX).



#### D. Ethylene Dimerization

Ethylene is rapidly dimerized to 1-butene in the presence of rhodium(I). Cramer (48, 50) has elucidated the reaction mechanism, which is illustrated in Fig. 7. Isomerization of the 1-butene to a mixture of 1- and 2-butenes also takes place. The thoroughly studied dimerization mechanism is significant inasmuch as several basic reactions of organometallic chemistry are illustrated in this process. This reaction is an excellent example of the critical importance of auxiliary ligands to catalytic activity. Halide ion is required for catalytic activity.

The planar bis(ethylene)-rhodium(I) complex (LXX) is the active catalyst. Oxidative addition of HCl to this unsaturated  $d^8$  complex affords the rhodium(III) hydride (LXXI) which rapidly yields the ethyl complex (LXXII). No direct evidence was found for the existence of the hydride (LXXI), but NMR evidence supports the existence of the ethyl complex (LXXII). These first two steps are rapid and reversible and provide a mechanism for deuterium exchange between the protons on ethylene and

the HCl. The octahedral ethylene complex (LXXII) is in equilibrium with dissociated ethylene. A solvent molecule S (either ethanol or water) is thought to take up the remaining coordination site to achieve normal octahedral coordination. The rate-determining step is the transformation

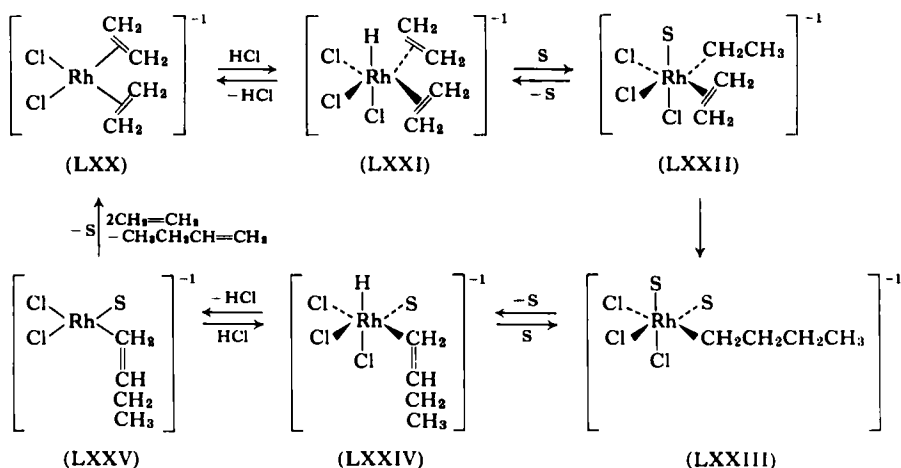


FIG. 7.

of the ethyl complex (LXXII) into the butyl complex (LXXIII). Analysis of kinetic and equilibrium data suggests that the activated complex has the stoichiometry exhibited by (LXXII). Activation parameters for this slow step are similar to those found in the  $\text{MeMn}(\text{CO})_5$  carbon monoxide insertion reaction. The rapid transformation of the butyl complex (LXXIII) into the hydridobutene complex (LXXIV) (reverse insertion) is followed by rapid reductive elimination of HCl to form a rhodium(I) butene complex (LXXV). Ethylene rapidly displaces butene from (LXXV). Part of the vital role which chloride ion plays in this mechanism may be to provide activation for the oxidative-addition step.

#### ACKNOWLEDGMENTS

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# Keto Derivatives of Group IV Organometalloids

A. G. BROOK

Department of Chemistry  
University of Toronto  
Toronto, Canada

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## I

## INTRODUCTION

Benzoyltriphenylsilane, the first reported example of a class of compound in which an acyl group is directly attached to a metalloid atom, was originally described in 1957 (1). The bright yellow color of this compound was remarkable when compared to its colorless carbon analog,  $\beta$ -benzpinacolone. This new class of carbon-functional organometalloid, involving silicon, germanium, and tin, now embraces several dozen members which have been shown to possess not only unusual spectral properties but unusual chemical behavior as well.

*A. Scope*

This review has been arbitrarily limited to those carbonyl compounds of silicon, germanium, and tin in which the carbonyl group is either directly attached to the metalloid atom or is separated from it by not more than a single intervening carbon atom. In these cases it is clearly evident that unusual interaction between the metalloid atom and carbonyl group exists, as evidenced by unusual spectral and/or chemical behavior. On the other hand when two or more carbon atoms separate the metalloid atom from the carbonyl group the available evidence indicates that no unusual interaction exists between the groups, and the compounds possess those properties normally associated with an organometalloid and a ketone, and are thus unexceptional. We will therefore be concerned with the methods of synthesis and the spectral and chemical properties of  $\alpha$ - and  $\beta$ -ketometalloid compounds, and an attempt will be made to interpret these data in terms of possible interactions between the metalloid atom, with its relatively low electronegativity and with its energetically available but empty *d* orbitals, and the carbonyl group.

Since research in this area is currently very active, the author has felt it desirable to incorporate recently completed, but as yet unpublished, findings from his own research group in the interests of presenting as accurate and current a picture of the field as possible.

*B. Nomenclature*

The nomenclature of metalloid carbonyl compounds is in a state of confusion. Compounds in which a metalloid atom, e.g., Si, is directly

attached to the carbonyl group (e.g.,  $\equiv\text{Si}-\text{CO}-\text{R}$ ) have been called  $\alpha$ -silyl ketones (2-6), silyl ketones (7, 8), and acylsilanes (e.g., benzoyltriphenylsilane) (9), all with some justification. Compounds in which a carbon atom separates the silicon atom from the carbonyl group have been called  $\beta$ -silyl ketones (10),  $\beta$ -ketosilanes (11, 12) and  $\alpha$ -ketosilanes (8).<sup>1</sup>

Individual members of the class of compounds where the metalloid is directly attached to the carbonyl group are unquestionably best named as "acylmetalloids" in virtually all cases (e.g., benzoyltrimethylsilane, acetyltriethylgermane), and as a class the names "acylsilane, acylgermane, and acylstannane (or acyltin)" seem quite appropriate; " $\alpha$ -ketosilane" is less acceptable, but is preferable to " $\alpha$ -silyl ketone." Similarly individual members of the class of compounds in which carbon, usually as a methylene group, separates silicon and the carbonyl group, may be named as substituted silanes (e.g., phenacyltriphenylsilane,  $\text{PhCOCH}_2\text{SiPh}_3$ ) where the substituents are readily named, or as substituted ketones (e.g., trimethylsilylacetone,  $\text{Me}_3\text{SiCH}_2\text{COCH}_3$ ). As a class it is recommended that these compounds be described as " $\beta$ -ketosilanes" which seems less confusing than the alternative " $\beta$ -oxosilanes." Further separation of the two groups then leads to possible descriptions of compounds as  $\gamma$ - or  $\delta$ -ketosilanes, etc.

Similar terminology would apply to the related germanes and stannanes. The suggested nomenclature is summarized below.<sup>2</sup>

Structure <sup>a</sup>	Nomenclature of class
$\equiv\text{M}-\text{CO}-\text{R}$	Acylsilane, -germane, -stannane
$\equiv\text{M}-\text{CH}_2-\text{CO}-\text{R}$	$\beta$ -Ketosilane, -germane, -stannane
$\equiv\text{M}-\text{CH}_2\text{CH}_2-\text{CO}-\text{R}$	$\gamma$ -Ketosilane, -germane, -stannane
$\equiv\text{M}-\text{CO}-\text{M}\equiv$	Bis(silyl) ketone, bis(germyl) ketone, etc.

<sup>a</sup> Throughout this article M will be used to represent some or all of C, Si, Ge, Sn, and Pb.

<sup>1</sup> The use of  $\alpha$  and  $\beta$  probably arose in some cases by analogy with the description of the behavior of compounds such as  $\equiv\text{Si}-\text{CH}_2-\text{Cl}$  as involving an " $\alpha$ -silicon" effect (13).

<sup>2</sup> The author is grateful to a number of friends and colleagues in the field of organosilicon chemistry for useful comments on this subject.

## II

**SYNTHESIS OF ACYLSILANES, ACYLGERMANES,  
AND ACYLSTANNANES**

Methods for synthesizing carbon ketones are legion. Early attempts to apply the more common of these to the synthesis of acylsilanes failed, generally because of the relative instability of the acylsilane to the reagents or reaction conditions, products resulting from cleavage of the carbonyl-metalloid bond by hydrolysis being commonly found. The first known synthesis of an acylsilane involved the coupling of triphenylsilylpotassium with benzoyl chloride at low temperature (1). The very low yield of the yellow product (6%) and the comparable yields from the coupling of silyllithium reagents with acetyl chloride to give acetyltriphenylsilane (15) indicate that this is not a very useful method for the synthesis of acylsilanes, although as will be noted in Section II,F, the comparable coupling of germyllithium with benzoyl chlorides is an excellent route to acylgermanes (6). Continued investigations on methods of acylsilane synthesis involving relatively mild conditions have led to four generally successful synthetic routes as follows:

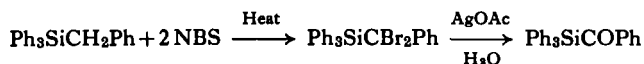
- (A) Hydrolysis of geminal dihalides
- (B) Oxidations of  $\alpha$ -hydroxymetalloids with chromic acid
- (C) Oxidations of  $\alpha$ -hydroxymetalloids with reagents containing dimethyl sulfoxide
- (D) Hydrolysis of 2-metalloidal-1,3-dithianes.

These methods are described in the following sections primarily from the point of view of acylsilane synthesis, but applications to acylgermanes and acylstannanes are given where appropriate. Following a section on Miscellaneous syntheses (E), a short section on methods specifically suited to acylgermanes is included. Tables are given listing the methods of preparation and the melting point or boiling point of all known acyl-metalloids together with references. Table I includes data for all known acylsilanes, and Table II gives data for acylgermanes and acylstannanes.

**A. Hydrolysis of Geminal Dihalides**

The first successful route to benzoyltriphenylsilane involved dibromination of benzyltriphenylsilane with *N*-bromosuccinimide. Mild hydrolysis of the resulting  $\alpha,\alpha$ -dibromobenzyltriphenylsilane by stirring the solution

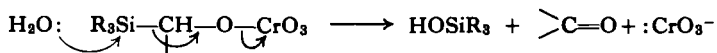
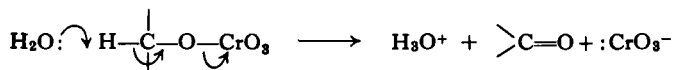
in acetone-ethanol-water with silver acetate for 16 hours, preferably in the dark, gave the acylsilane in high yield.



Subsequently, a variety of other benzoyl- (21) and *p*-substituted benzoyl-silanes (9) and -germanes (2) have been similarly prepared by this method (see Tables I and II, Method A) but the method is obviously restricted to benzyl- and allylsilanes and -germanes where geminal dihalides can be prepared. Silver trifluoroacetate has also been used for the hydrolysis, as have other solvent combinations in addition to that mentioned above (9, 21).

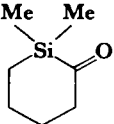
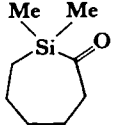
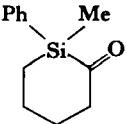
### B. Oxidation of $\alpha$ -Hydroxymetalloids with Chromic Acid

Since the oxidation of secondary alcohols to ketones by any of a wide variety of oxidizing agents is a commonly successful route, it might have been expected that the oxidation of the corresponding  $\alpha$ -hydroxysilanes to acylsilanes would be a generally useful reaction. In fact, while reduction of the oxidizing agent does occur using potassium permanganate, chromic acid, chromic oxide in pyridine or *tert*-butyl alcohol, etc., the major products obtained are those expected from hydrolysis of the desired ketone (1). As shown below, oxidation of a carbinol occurs by nucleophilic attack on the hydrogen atom  $\beta$  to chromium of a chromate ester intermediate. With a hydroxysilane, nucleophilic attack on silicon leading to silanol and aldehyde would be an even more likely process, the susceptibility of silicon to nucleophilic attack being well known (20).



Some success in oxidizing  $\alpha$ -hydroxysilanes to acylsilanes was obtained using chromic oxide in aqueous sulfuric acid-acetone, 60–70% yields of acetyl- and propionyltriphenylsilane having been obtained (20, 23) (Table I, Method B). However, other carbinols, e.g., 1,1-diphenylsila-2-cyclohexanol, and bis(triphenylgermyl)carbinol, under similar conditions, failed to give significant amounts of ketone (20).

TABLE I  
ACYLSILANES

Empirical formula	Compound	M.p. or b.p./mm Hg <sup>a</sup> (°C)	Method of preparation <sup>b</sup>	References
C <sub>5</sub> H <sub>12</sub> OSi	Me <sub>3</sub> SiCOMe	113°/760	C, D D	7 5
C <sub>7</sub> H <sub>14</sub> OSi		75°/115 44°/3.6 ( <i>n</i> <sub>D</sub> <sup>25</sup> = 1.4636)	C D	17
C <sub>8</sub> H <sub>16</sub> OSi		43°/1.5 ( <i>n</i> <sub>D</sub> <sup>25</sup> = 1.4707)	D	17
C <sub>8</sub> H <sub>18</sub> OSi	Me <sub>3</sub> SiCOCMe <sub>3</sub>	76°–77°/66 ( <i>n</i> <sub>D</sub> <sup>20</sup> = 1.4266)	D	5
C <sub>10</sub> H <sub>14</sub> OSi	Me <sub>3</sub> SiCOPh	42°–44°/0.02 ( <i>n</i> <sub>D</sub> <sup>25</sup> = 1.5170)	A, D	2, 5
C <sub>11</sub> H <sub>16</sub> OSi	Me <sub>3</sub> SiCOCH <sub>2</sub> Ph	50°/0.08 ( <i>n</i> <sub>D</sub> <sup>22</sup> = 1.5043)	D	19
C <sub>12</sub> H <sub>16</sub> OSi		83°/0.2 [α] <sub>D</sub> <sup>25</sup> = –160°, <i>n</i> <sub>D</sub> <sup>25</sup> = 1.5448	C, D	17
C <sub>15</sub> H <sub>16</sub> OSi	Me <sub>2</sub> PhSiCOPh	54°–55° 100°–102°/0.04	A	2

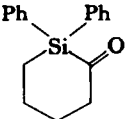
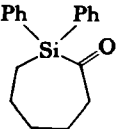
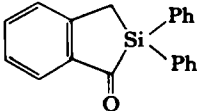
$C_{17}H_{18}OSi$		$63^{\circ}-65^{\circ}$	B, C, D	17, 20
$C_{18}H_{20}OSi$		Oil not distilled	D	17
$C_{19}H_{18}O_2Si$	$Ph_2(OH)SiCOPh$	$97^{\circ}-99^{\circ}$	A	21
$C_{19}H_{18}OSi$	$1-NpPhMeSiCOMe$	$83^{\circ}-84^{\circ}$ $[\alpha]_D = -40^{\circ}$	D	7
$C_{20}H_{16}OSi$		$102.5^{\circ}-103.5^{\circ}$	$E^c$	22
$C_{20}H_{18}OSi$	$Ph_3SiCOCH_3$	$126^{\circ}-127^{\circ}$	B C D $E^d$	23 24, 25, 26 7 15
$C_{20}H_{18}OSi$	$Ph_2MeSiCOPh$	$158^{\circ}/0.08\text{ mm}$ $(n_D^{20} = 1.6185)$	A	2
$C_{20}H_{18}O_2Si$	$Ph_2(OMe)SiCOPh$	Impure	A	21
$C_{21}H_{20}OSi$	$Ph_3SiCOCH_2CH_3$	$105^{\circ}-106^{\circ}$	B	20
$C_{23}H_{24}OSi$	$Ph_3SiCOC(CH_3)_3$		$E^d$	27
$C_{24}H_{20}OSi$	$1-NpPhMeSiCOPh$	$84^{\circ}-86^{\circ}$ $[\alpha]_D = +6.20^{\circ}$	D, A	7, 28
$C_{25}H_{17}Cl_3OSi$	$(p\text{-}ClC_6H_4)_3SiCOPh$	$129^{\circ}-131^{\circ}$ racemic	A	28
$C_{25}H_{19}BrOSi$	$Ph_3SiCOC_6H_4Br\text{-}p$	$111^{\circ}-111.5^{\circ}$ $116^{\circ}-117^{\circ}$	A A	9 9



TABLE I—(continued)

Empirical formula	Compound	M.p. or b.p./mm Hg <sup>a</sup> (°C)	Method of preparation <sup>b</sup>	References
C <sub>25</sub> H <sub>19</sub> ClOSi	Ph <sub>3</sub> SiCOC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	93°–95°	A	9
C <sub>25</sub> H <sub>19</sub> FOSi	Ph <sub>3</sub> SiCOC <sub>6</sub> H <sub>4</sub> F- <i>p</i>	116°–118°	A	9
C <sub>25</sub> H <sub>19</sub> NO <sub>3</sub> Si	Ph <sub>3</sub> SiCOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	155°–157°	A	9
C <sub>25</sub> H <sub>20</sub> OSi	Ph <sub>3</sub> SiCOPh	102°–103°	A, B, D	1, 7, 23
C <sub>26</sub> H <sub>20</sub> Br <sub>2</sub> OSi	PhCOSiPh <sub>2</sub> CBr <sub>2</sub> Ph	107°–109°	A	21
C <sub>26</sub> H <sub>20</sub> BrClOSi	PhCOSiPh <sub>2</sub> CBrClPh	118°–120°	A	21
C <sub>25</sub> H <sub>20</sub> O <sub>2</sub> Si	PhCOSiPh <sub>2</sub> COPh	Impure	A	21
C <sub>26</sub> H <sub>21</sub> BrOSi	PhCOSiPh <sub>2</sub> CHBrPh	90°–92°	A	21
C <sub>26</sub> H <sub>21</sub> ClOSi	PhCOSiPh <sub>2</sub> CHClPh	100°–101°	A	21
C <sub>26</sub> H <sub>22</sub> OSi	Ph <sub>3</sub> SiCOCH <sub>2</sub> Ph	94°–95°	D	19
C <sub>26</sub> H <sub>22</sub> O <sub>2</sub> Si	Ph <sub>3</sub> SiCOC <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	131.5°–132.5°	A	9
C <sub>28</sub> H <sub>17</sub> F <sub>9</sub> OSi	( <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCOPh	79°–80°	A	9
C <sub>29</sub> H <sub>28</sub> OSi	Ph <sub>3</sub> SiCOC <sub>6</sub> H <sub>4</sub> - <i>tert</i> -Bu- <i>p</i>	151°–152°	A	9
C <sub>32</sub> H <sub>28</sub> OSi <sub>2</sub>	Ph <sub>3</sub> SiSiPh <sub>2</sub> COCH <sub>3</sub>	165°–167°	D	77
C <sub>37</sub> H <sub>30</sub> OSi <sub>2</sub>	Ph <sub>3</sub> SiSiPh <sub>2</sub> COPh	198.5°–200°	A	77
C <sub>37</sub> H <sub>44</sub> OSi	( <i>p</i> - <i>tert</i> -BuC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCOPh	140°–142°	A	30
C <sub>40</sub> H <sub>34</sub> OSi <sub>2</sub>	Ph <sub>3</sub> SiCOCH=C(Me)SiPh <sub>3</sub>	160°–165°	E <sup>c</sup>	23

<sup>a</sup> If no number referring to pressure is given, the value listed is a melting point.

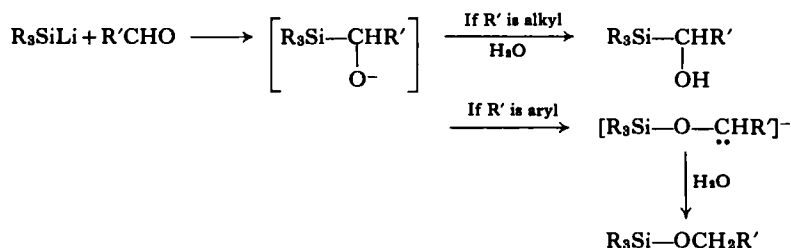
<sup>b</sup> Methods of preparation: A, hydrolysis of geminal dihalide; B, chromic acid oxidation of  $\alpha$ -hydroxysilane; C, oxidation of  $\alpha$ -hydroxysilane with reagent containing DMSO (dimethyl sulfoxide); D, via 1,3-dithiane and its hydrolysis; E, miscellaneous.

<sup>c</sup> Carbinol + *N*-bromosuccinimide-CaCO<sub>3</sub>.

<sup>d</sup> Ph<sub>3</sub>SiLi + RCOCl.

<sup>e</sup> Ph<sub>3</sub>SiCOCH<sub>3</sub> + PhMgBr—Aldol condensation?

Apart from problems of silicon-carbon bond cleavage, a second difficulty limiting the utility of this synthesis is that of obtaining the appropriate silylcarbinol. Whereas  $\alpha$ -hydroxysilanes can be isolated from the reaction of silylmetallic reagents with aliphatic aldehydes (33, 34), the initial adducts from reaction with aromatic aldehydes such as benzaldehyde rearrange to the isomeric silyl ethers too rapidly for any silylcarbinol to be isolated (33, 35). The mechanism of this reaction, summarized below, has been investigated in detail (30).



In addition, since trialkylsilyllithium reagents have not been accessible (36) and arylsilyllithium reagents are not always easily prepared, this represents a further restriction to the variety of silylcarbinols readily available.

Some of the problems enumerated above do not occur in the synthesis of germylcarbinols. Thus germylcarbinols, formed from reaction of aldehydes with germyllithium reagents (2) which themselves are easily prepared by metalation of the corresponding germane (6), do not undergo a germylcarbinol to germyl ether type of rearrangement so that, in principle, either alkyl or aryl aldehydes can be used (2). Chromic acid oxidation of germylcarbinols has not been widely investigated..

### C. Oxidations with Dimethyl Sulfoxide

The oxidation methods so far discussed clearly leave room for improvement and considerable success has attended use of reagents employing dimethyl sulfoxide (DMSO), as originally described by Pfitzner and Moffatt (37). A general review of the applications of this oxidizing agent has recently appeared (38).

Of the various systems described, that using dicyclohexylcarbodiimide (DCC) with pyridinium trifluoroacetate has been most investigated (7, 20). The DMSO-DCC-pyridinium trifluoroacetate system gave virtually

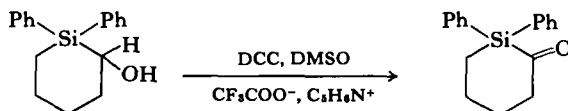
TABLE II  
ACYLGERMANES AND ACYLSTANNANES

Empirical formula	Compound	M.p. or b.p./mm Hg <sup>a</sup> (°C)	Method of preparation <sup>b</sup>	References
C <sub>8</sub> H <sub>18</sub> GeO	Et <sub>3</sub> GeCOMe	Undistilled	D	7
C <sub>10</sub> H <sub>14</sub> GeO	Me <sub>3</sub> GeCOPh	54°/0.28 ( $n_D^{25} = 1.5364$ )	A	31
C <sub>13</sub> H <sub>20</sub> GeO	Et <sub>3</sub> GeCOPh	82°–83°/0.15	D	7
C <sub>20</sub> H <sub>18</sub> GeO	Ph <sub>3</sub> GeCOMe	122°–123°	B, D	7, 32
C <sub>23</sub> H <sub>24</sub> GeO	Ph <sub>3</sub> GeCOCMe <sub>3</sub>	103°–105°	E	27
C <sub>24</sub> H <sub>20</sub> GeO	1-NpPhMeGeCOPh	132°–134° racemic	C	29
C <sub>25</sub> H <sub>19</sub> FGeO	Ph <sub>3</sub> GeCOC <sub>6</sub> H <sub>4</sub> F- <i>p</i>	118°–120°	E	6
C <sub>25</sub> H <sub>20</sub> GeO	Ph <sub>3</sub> GeCOPh	101°–102°	A, B, C	2, 23, 25
			E	6
C <sub>26</sub> H <sub>19</sub> F <sub>3</sub> GeO	Ph <sub>3</sub> GeCOC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> - <i>p</i>	116°–118°	E	6
C <sub>26</sub> H <sub>22</sub> GeO <sub>2</sub>	Ph <sub>3</sub> GeCOC <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	136°–138.5°	E	6
C <sub>20</sub> H <sub>18</sub> OSn	Ph <sub>3</sub> SnCOMe	—	F	32
C <sub>23</sub> H <sub>24</sub> OSn	Ph <sub>3</sub> SnCOCMe <sub>3</sub>	—	F	27
C <sub>25</sub> H <sub>20</sub> OSn	Ph <sub>3</sub> SnCOPh	—	F	27

<sup>a</sup> Numbers are melting points unless data for pressure are given.

<sup>b</sup> Method of preparation: A, hydrolysis of geminal dihalide; B, oxidation of  $\alpha$ -hydroxygermane with chromic acid; C, oxidation of  $\alpha$ -hydroxygermane with reagent containing DMSO (dimethyl sulfoxide); D, hydrolysis of 1,3-dithiane; E, R<sub>3</sub>GeLi + RCOCl in THF at –70°C; F, Ph<sub>3</sub>SnLi + RCOCl at –78°C.

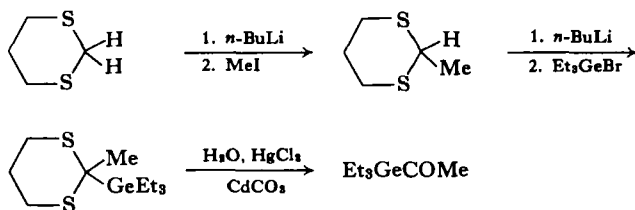
quantitative yields of benzoyltriphenylsilane (25), benzoyltriphenylgermane (25), and 1,1-diphenylsilacyclohexanone-2 (20), and substantial yields of acetyltrimethylsilane (7), bis(triphenylsilyl) and bis(triphenylgermyl) ketones (16) from the corresponding carbinols.



However, the separation of the ketone from the dicyclohexylurea formed in the reaction is frequently a serious experimental problem. Use of phosphoric, phosphorous, or cyanoacetic acid in lieu of pyridinium trifluoroacetate gave inferior yields. Limited investigation of the dimethyl sulfoxide-acetic anhydride reagent has shown it to be superior in oxidations of triphenylsilylmethylcarbinol, triphenylsilylethylcarbinol, and 1,1-diphenylsila-2-cyclohexanol, giving the corresponding ketones in 60–70% yields (17, 24) since no separation problems are encountered.

#### D. Hydrolysis of 2,2-Disubstituted-1,3-dithianes

In 1965 Corey and Seebach published a new synthetic route to ketones via 1,3-dithianes (39). The potentiality of this elegant method for the synthesis of sensitive compounds was immediately recognized (7, 18) and a variety of hitherto unobtainable ketones was synthesized such as 1-naphthylphenylmethylacetylsilane, acetyltriethylgermane, and *tert*-butyl trimethylsilyl ketone. The method takes advantage of the ready metalation of 1,3-dithiane and the reactivity of the resulting anion as a nucleophile toward reactive carbon, silicon, or germanium halides. The synthesis of acetyltriethylgermane is illustrated.

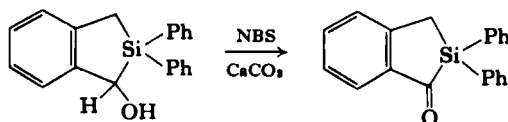


While a very wide variety of 2-metalloidal-1,3-dithianes can be prepared, even including bis(silyl), bis(germyl), or mixed metalloidal compounds,

certain limitations have been found in ketone synthesis. The difficult slow step is the hydrolysis of the dithiane, which is best carried out using aqueous mercuric chloride. Addition of several moles of cadmium carbonate seems to minimize hydrolysis of the ketone, presumably by maintaining a neutral pH (7). Even these mild conditions sometimes lead to low yields of the ketones, probably due to hydrolysis. In addition no success has attended efforts to synthesize acylstannanes by this route, and attempts to obtain some ketones such as bis(triphenylsilyl) ketone by hydrolysis of the appropriate dithiane have failed completely. In fact triarylsilyldithianes appear to hydrolyze much more slowly than their alkyl counterparts, probably because of electronic effects. Ketones synthesized by hydrolysis of dithianes are listed in Tables I and II, under Method D.

### E. Miscellaneous Syntheses

In a few cases,  $\alpha$ -hydroxysilanes have been converted into acylsilanes by oxidations using *N*-bromosuccinimide. Thus 3:4-benzo-2-hydroxy-1,1-diphenyl-1-silacyclopent-3-ene was converted to the corresponding ketone (22) in the presence of calcium carbonate as hydrogen bromide acceptor.



Ozonization of vinylmetalloids does not appear to yield acylsilanes readily. The formation of trimethylsilylformaldehyde ( $\text{Me}_3\text{SiCHO}$ ) during hydrolysis of the ozonide of vinyltrimethylsilane was postulated but only decomposition products were isolated (40).

Gilman has recently reported that silylcopper and germylcopper compounds couple with acid chlorides to give acylmetalloids in good yield.

### F. Acylgermanes and Acylstannanes

While the preceding sections were written primarily from the point of view of acylsilane synthesis, identical methods have been successfully employed in the synthesis of acylgermanes.

In addition to these general methods, Nicholson and Allred (6) have found that the addition of germyllithium reagents to aromatic acid chlorides at low temperature leads to excellent yields of acylgermanes. However, the

coupling route with aliphatic acid chlorides did not lead to alkyl germyl ketones, although Peddle (32) reported successful coupling of triphenylgermyllithium with acetyl chloride and pivalyl chloride at  $-70^{\circ}\text{C}$ . A virtue of this route lies in the fact that germyllithium reagents are readily prepared by metalation of the corresponding germane with *n*-butyllithium; in the analogous silicon case, coupling occurs, so that the silyllithium reagent must be prepared in other ways.



The synthesis of acetyltriphenyltin has been reported by coupling of triphenyltinlithium with acetyl chloride at  $-70^{\circ}\text{C}$  (32); attempts to form benzoylstannanes by coupling with benzoyl chloride gave a yellow color suggestive of ketone formation, but no ketone has been isolated (25, 27).

### III

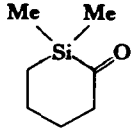
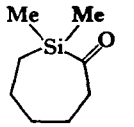
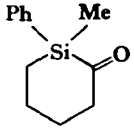
#### SPECTRA OF ACYLMETALLOIDS

Perhaps the most unusual features of acylmetalloids are their spectral properties, especially when considered with reference to their carbon analogs. Both infrared and ultraviolet absorption occur at significantly longer wavelengths in acylmetalloids relative to their carbon analogs and all benzoylmetalloids are in fact yellow, while their carbon analogs are colorless. Several explanations have been proposed to account for these effects, as will be mentioned below.

##### *A. Infrared Absorption Spectra*

Aliphatic ketones such as acetone and cyclohexanone have carbonyl stretching infrared absorption at about  $5.84\ \mu$  ( $1712\ \text{cm}^{-1}$ ). When conjugated with an aromatic ring the wavelength increases to about  $5.91\ \mu$  ( $1692\ \text{cm}^{-1}$ ). By contrast, as indicated in Table III which lists the infrared and ultraviolet spectral properties of all known acylsilanes, and Table IV, which lists the same properties for acylgermanes and acylstannanes, strong bands attributed to carbonyl stretching were found for silyl alkyl ketones ( $\text{Si}-\text{CO}-\text{alkyl}$ ) at about  $6.08\ \mu$  ( $1645\ \text{cm}^{-1}$ ) and for silyl aryl ketones ( $\text{Si}-\text{CO}-\text{aryl}$ ) in the vicinity of  $6.18\ \mu$  ( $1618\ \text{cm}^{-1}$ ) (2, 7). The analogous germanium compounds absorb at about  $6.0\ \mu$  ( $1667\ \text{cm}^{-1}$ ) and  $6.14\ \mu$  ( $1629\ \text{cm}^{-1}$ ) (7, 32). A linear correlation of the Hammett constants

TABLE III  
SPECTRAL PROPERTIES OF ACYLSILANES

Empirical formula	Compound	Infrared <sup>a</sup> C=O		Ultraviolet <sup>b</sup>	
		( $\mu$ )	( $\text{cm}^{-1}$ )	Solvent	$\lambda_{\text{max}}(\epsilon)$
C <sub>5</sub> H <sub>12</sub> OSi	Me <sub>3</sub> SiCOMe	6.08	1645	Heptane C <sub>6</sub> H <sub>12</sub>	195(4,200), 210(s), 323(18), 333(34), 346(62), 358(100), 372(126), 388(93)
C <sub>7</sub> H <sub>14</sub> OSi		6.06	1650	C <sub>6</sub> H <sub>12</sub>	365(73), 378(100), 394(90)
C <sub>8</sub> H <sub>16</sub> OSi		6.11	1636	C <sub>6</sub> H <sub>12</sub>	338(25)(s), 350(51)(s), 364(88), 380(112), 398(80)
C <sub>8</sub> H <sub>18</sub> OSi	Me <sub>3</sub> SiCOCMe <sub>3</sub>	6.11	1636	C <sub>6</sub> H <sub>12</sub>	367(200)
C <sub>10</sub> H <sub>14</sub> OSi	Me <sub>3</sub> SiCOPh	6.18	1618	Heptane EtOH	198(30,200), 251(11,700), 281(s), 424(101) <sup>d</sup> 252(11,700), 402(117), 413(118)
C <sub>11</sub> H <sub>16</sub> OSi	Me <sub>3</sub> SiCOCH <sub>2</sub> Ph	6.04, 6.09 <sup>c</sup>	1656, 1642	C <sub>6</sub> H <sub>12</sub>	224(5,800), 259(s)(250), 363(s)(80), 375(94), 389(s)(70)
C <sub>12</sub> H <sub>16</sub> OSi		6.08	1645	C <sub>6</sub> H <sub>12</sub>	219(6,730), 264(s)(442), 272(264), 336(s)(157), 361(217), 390(204)
C <sub>15</sub> H <sub>16</sub> OSi	Me <sub>2</sub> PhSiCOPh	6.18	1618	EtOH	255(13,900), 403(s)(200), 415(216)

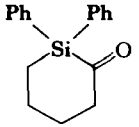
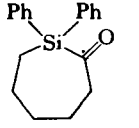
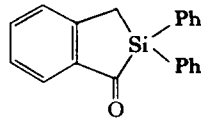
C <sub>17</sub> H <sub>18</sub> OSi		6.07	1647	C <sub>6</sub> H <sub>12</sub>	261(520), 266(1,225), 273(834), 367(s)(196), 383(284), 396(265)
C <sub>18</sub> H <sub>20</sub> OSi		6.11	1636	—	—
C <sub>19</sub> H <sub>16</sub> O <sub>2</sub> Si	Ph <sub>2</sub> (OH)SiCOPh	6.19	1616	EtOH	257(16,900), 405(s), 415(318)
C <sub>19</sub> H <sub>18</sub> OSi	1-NpPhMeSiCOMe	6.09	1642	C <sub>6</sub> H <sub>12</sub>	225(48,000), 229(51,000), 273(6,700), 288(8,300), 298(5,800), 337(104), 349(195), 361(318)
C <sub>20</sub> H <sub>16</sub> OSi		6.08	1645	C <sub>6</sub> H <sub>12</sub>	223(37,150), 260(16,980), 268(15,850), 296(19,770), 385(25), 404(63), 425(151), 448(282), 476(229)
C <sub>20</sub> H <sub>18</sub> OSi	Ph <sub>2</sub> MeSiCOPh	6.18	1618	EtOH	256(12,200), 403(s)(210), 417(235)
C <sub>20</sub> H <sub>18</sub> OSi	Ph <sub>3</sub> SiCOMe	6.08	1645	Heptane	195(110,000), 273(706), 376(406) <sup>d</sup>
				EtOH	260(1513), 265(1493), 272(1058), 360(324), 372(366), 384(239)
C <sub>20</sub> H <sub>18</sub> O <sub>2</sub> Si	MeOPh <sub>2</sub> SiCOPh	6.19	1616	EtOH	405–415 <sup>e</sup>
C <sub>21</sub> H <sub>20</sub> OSi	Ph <sub>3</sub> SiCOEt	6.08	1645	EtOH	260(1,580), 265(1,485), 272(987), 355(233), 370(302), 385(243)
C <sub>24</sub> H <sub>20</sub> OSi	1-NpPhMeSiCOPh	6.18	1618	C <sub>6</sub> H <sub>12</sub>	257(15,600), 280(10,050), 297(s)(7,040), 386(115), 404(228), 423(301), 445(181)
C <sub>25</sub> H <sub>17</sub> Cl <sub>3</sub> OSi	( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCOPh	6.18	1617	C <sub>6</sub> H <sub>12</sub>	229(38,400), 257(s)(19,600), 387(s)(149), 403(227), 422(363), 442(230)
C <sub>25</sub> H <sub>19</sub> BrOSi	Ph <sub>3</sub> SiCOC <sub>6</sub> H <sub>4</sub> Br- <i>p</i>	6.18	1618	C <sub>6</sub> H <sub>12</sub>	271(21,700), 390(s)(117), 407(216), 428(271), 448(158)



TABLE III—*continued*

Empirical formula	Compound	Infrared <sup>a</sup> C=O		Solvent	Ultraviolet <sup>b</sup>	
		( $\mu$ )	( $\text{cm}^{-1}$ )		$\lambda_{\text{max}}(\epsilon)$	
$\text{C}_{25}\text{H}_{19}\text{ClOSi}$	$\text{Ph}_3\text{SiCOC}_6\text{H}_4\text{Cl-}p$	6.18	1618	$\text{C}_6\text{H}_{12}$	268(18,400), 391(s)(117), 408(217), 427(273), 448(159)	
$\text{C}_{25}\text{H}_{19}\text{FOSi}$	$\text{Ph}_3\text{SiCOC}_6\text{H}_4\text{F-}p$	6.18	1618	$\text{C}_6\text{H}_{12}$	260(13,700), 384(s)(119), 400(223), 419(290), 440(188)	
$\text{C}_{25}\text{H}_{19}\text{NO}_3\text{Si}$	$\text{Ph}_3\text{SiCOC}_6\text{H}_4\text{NO}_2\text{-}p$	6.16	1624	$\text{C}_6\text{H}_{12}$	266(17,800), 411(s)(132), 434(192), 448(192), 478(89)	
$\text{C}_{25}\text{H}_{20}\text{OSi}$	$\text{Ph}_3\text{SiCOPh}$	6.18	1618	$\text{C}_6\text{H}_{12}$	195(162,000), 257(16,200), 388(s)(118), 405(222), 424(292), 440(177)	
				EtOH	258(15,500), 403(264), 417(300)	
$\text{C}_{26}\text{H}_{20}\text{Br}_2\text{OSi}$	$\text{PhCOSiPh}_2\text{CBr}_2\text{Ph}$	6.18	1617	EtOH	259(18,600), 405(s)(233), 416(265)	
$\text{C}_{26}\text{H}_{20}\text{BrClOSi}$	$\text{PhCOSiPh}_2\text{CBrClPh}$	6.18	1617	—	—	
$\text{C}_{26}\text{H}_{20}\text{O}_2\text{Si}$	$\text{PhCOSiPh}_2\text{COPh}$	6.18, 5.97	1617, 1675	EtOH	258(24,100), 405(s)(233), 416(244)	
$\text{C}_{26}\text{H}_{21}\text{BrOSi}$	$\text{PhCOSiPh}_2\text{CHBrPh}$	6.18	1617	—	—	
$\text{C}_{26}\text{H}_{21}\text{ClOSi}$	$\text{PhCOSiPh}_2\text{CHClPh}$	6.18	1617	—	—	
$\text{C}_{26}\text{H}_{22}\text{OSi}$	$\text{Ph}_3\text{SiCOCH}_2\text{Ph}$	6.05, 6.10 <sup>c</sup>	1653, 1639	$\text{C}_6\text{H}_{12}$	218(29,000), 260(s)(2,900), 266(2,900), 274(1,870), 359(s)(168), 373(244), 386(238)	

C <sub>26</sub> H <sub>22</sub> O <sub>2</sub> Si	Ph <sub>3</sub> SiCOC <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	6.19	1616	C <sub>6</sub> H <sub>12</sub>	290(20,800), 298(s)(17,400), 380(s)(132), 396(246), 414(335), 434(232)
C <sub>28</sub> H <sub>17</sub> F <sub>9</sub> OSi	( <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCOPh	6.18	1617	C <sub>6</sub> H <sub>12</sub>	266(17,250), 384(s)(133), 401(239), 418(314), 438(201)
C <sub>28</sub> H <sub>26</sub> OSi	( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCOPh	6.18	1617	C <sub>6</sub> H <sub>12</sub>	263 404, 423, 446 <sup>e</sup>
C <sub>29</sub> H <sub>28</sub> OSi	Ph <sub>3</sub> SiCOC <sub>6</sub> H <sub>4</sub> - <i>tert</i> -Bu- <i>p</i>	6.19	1616	C <sub>6</sub> H <sub>12</sub>	269(19,800), 386(s)(120), 403(227), 421(305), 442(200)
C <sub>32</sub> H <sub>28</sub> OSi <sub>2</sub>	Ph <sub>3</sub> SiSiPh <sub>2</sub> COMe	6.09	1642	C <sub>6</sub> H <sub>12</sub>	219(40,200), 245(s)(22,900), 268(s)(9,250), 275(s)(5,700), 338(s)(116), 351(s)(228), 363(380), 378(490), 393(396)
C <sub>37</sub> H <sub>30</sub> OSi <sub>2</sub>	Ph <sub>3</sub> SiSiPh <sub>2</sub> COPh	6.19	1616	C <sub>6</sub> H <sub>12</sub>	216(30,500), 244(48,600), 389(131), 407(262), 423(342), 445(234)
C <sub>37</sub> H <sub>44</sub> OSi	( <i>p</i> - <i>tert</i> -BuC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCOPh	6.18	1618	C <sub>6</sub> H <sub>12</sub>	227.5(38,000), 256(17,700), 407(286), 427(400), 448(250)
C <sub>40</sub> H <sub>34</sub> OSi <sub>2</sub>	Ph <sub>3</sub> SiCOCH=C(Me)SiPh <sub>3</sub>	6.14	1629	EtOH	228.5(39,700), 258(15,650), 420(346)
				EtOH	249(21,300), 255(23,600), 260(23,300), 460(322)

<sup>a</sup> Solvent for infrared measurement was CCl<sub>4</sub>.

<sup>b</sup> s = shoulder.

<sup>c</sup> Doublet, probably due to Fermi resonance.

<sup>d</sup> Band contains appreciable fine structure.

<sup>e</sup> Compound impure so extinction coefficient unknown.

TABLE IV  
SPECTRAL PROPERTIES OF ACYLGERMANES AND ACYLSTANNANES

Empirical formula	Compound	Infrared <sup>a</sup> C=O		Ultraviolet	
		( $\mu$ )	( $\text{cm}^{-1}$ )	Solvent	$\lambda_{\text{max}}(\epsilon)$
C <sub>8</sub> H <sub>18</sub> GeO	Et <sub>3</sub> GeCOMe	6.04	1656	C <sub>6</sub> H <sub>12</sub>	314(s)(15), 325(s)(34), 340(s)(76), 352(129), 365(173), 380(143)
C <sub>10</sub> H <sub>14</sub> GeO	Me <sub>3</sub> GeCOPh	6.14	1629	EtOH	252(10,700), 412(120) <sup>b</sup>
C <sub>13</sub> H <sub>20</sub> GeO	Et <sub>3</sub> GeCOPh	6.14	1629	C <sub>6</sub> H <sub>12</sub>	274(s)(1,100), 282(s)(1050), 292(s)(634), 409(s)(131), 424(151), 443(98)
C <sub>20</sub> H <sub>18</sub> GeO	Ph <sub>3</sub> GeCOMe	6.00	1669	C <sub>6</sub> H <sub>12</sub>	192(91,000), 260(s)(1,445), 265(s)(1,161), 271(s)(743), 329(s)(106), 341(s)(186), 352(298), 366(385), 380(310)
C <sub>24</sub> H <sub>20</sub> GeO	1-NpPhMeGeCOPh	6.14	1629	C <sub>6</sub> H <sub>12</sub>	251(13,200), 283(8,100), 288(6,400), 380(101), 400(166), 416(202), 433(s)(124)
C <sub>25</sub> H <sub>19</sub> GeFO	Ph <sub>3</sub> GeCOC <sub>6</sub> H <sub>4</sub> F- <i>p</i>	6.14	1628	Heptane	375(s)(101), 396(196), 413(243), 436(s)(141)
C <sub>25</sub> H <sub>20</sub> GeO	Ph <sub>3</sub> GeCOPh	6.14	1629	Heptane	193(56,100), 254(16,200), 401(173), 417(210), 440(123)
				EtOH	257(17,100), 403(262), 415(306) <sup>b</sup>
C <sub>26</sub> H <sub>19</sub> GeF <sub>3</sub> O	Ph <sub>3</sub> GeCOC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> - <i>p</i>	6.11	1637	Heptane	416(162), 430(178), 458(s)(91)
C <sub>26</sub> H <sub>22</sub> GeO <sub>2</sub>	Ph <sub>3</sub> GeCOC <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	6.14	1628	Heptane	389(218), 406(280), 424(189)
C <sub>20</sub> H <sub>18</sub> OSn	Ph <sub>3</sub> SnCOMe	6.00	1670	Heptane	363(s), 375, 391 <sup>c</sup>
C <sub>23</sub> H <sub>24</sub> OSn	Ph <sub>3</sub> SnCOCMe <sub>3</sub>	6.04	1655	Heptane	376 <sup>c</sup>
C <sub>25</sub> H <sub>20</sub> OSn	Ph <sub>3</sub> SnCOPh	6.15	1627	Heptane	435 <sup>c</sup>

<sup>a</sup> Infrared spectra run in CCl<sub>4</sub>.

<sup>b</sup> Band has considerable fine structure.

<sup>c</sup> Compound unstable so extinction coefficient unknown.

for *p*-substituents on the aromatic ring with the carbonyl absorption frequency has been observed (9). The position of carbonyl absorption is not altered detectably by changing the type of groups attached to the metalloid: trimethyl-, triphenyl-, and tris(*p*-substituted)phenylsilanes all absorb at the same wavelength (2, 9). The position of the carbonyl absorption of an acylsilane is also relatively insensitive to the polarity of the medium, compared to its carbon analog, but the shift to longer wavelengths on changing from carbon tetrachloride to acetonitrile is as expected for carbonyl stretching (2). The factors which affect the position of carbonyl stretching bands are many (41)—particularly pertinent in the present case would appear to be the low electronegativity of silicon (1.8) relative to carbon (2.5) and the larger mass of silicon. Whereas mesomeric effects acting in the ground state between the carbonyl group and the silicon *d* orbitals, i.e.,  $\pi(\pi-d)$  bonding, might be expected to lead to absorption at shorter wavelength, significant inductive release of electron density toward the carbonyl group, due to differences in electronegativity, would be anticipated to result in an increase in the wavelength, as is observed.

Pertinent to this argument are the data in Table V.

TABLE V  
INFRARED CARBONYL STRETCHING WAVELENGTHS OF METALLOID KETONES

M =	C		Si		Ge	
	( $\mu$ )	( $\text{cm}^{-1}$ )	( $\mu$ )	( $\text{cm}^{-1}$ )	( $\mu$ )	( $\text{cm}^{-1}$ )
$\text{Ph}_3\text{MCOPh}$	5.91	1692	6.18	1618	6.14	1629
$\text{Ph}_3\text{MCH}_2\text{COPh}$	5.89	1698	6.00	1667	6.02	1661
$\text{Ph}_3\text{MCH}_2\text{CH}_2\text{COPh}$	5.91	1692	5.91	1692	—	—

Acylsilanes and -germanes absorb at longer wavelengths than  $\beta$ -keto-metalloids and these absorb at longer wavelengths than the  $\gamma$ -keto compounds:  $\gamma$ -ketometalloids and all analogous carbon ketones absorb at the same wavelength. This behavior has been interpreted as consistent with a strong inductive release acting in acylmetalloys, which diminishes in strength in the  $\beta$ -ketometalloids, where it must operate through an intervening methylene group, and which has no observable effect through two methylene groups (10). However, the effect of  $\beta$ -substituents on carbonyl absorption wavelengths may also depend on their geometry relative to the

carbonyl group, as in the well known influence of equatorial, but not axial, halogen atoms on carbonyl stretching wavelengths (41). Such stereochemical effects have yet to be observed in these systems. Proposals of carbonyl-silicon interaction of a noninductive nature in  $\beta$ -ketosilanes have been made (42, 43) and are discussed in Section VIII, B.

The long-wavelength absorption of acylsilanes and -germanes infers a significantly polarized carbonyl group—thus it would be anticipated that these compounds might be significantly stronger bases than their less-polarized carbon analogs. This has indeed been found from two independent measurements (31): (a) the shift in carbonyl infrared wavelength on hydrogen bonding to phenol or methanol and (b) the effects on ultraviolet spectra of various concentrations of aqueous sulfuric acid. The results are shown below in Table VI.

TABLE VI  
RELATIVE BASICITIES OF ACYLMETALLOIDS

Compound	Relative basicity		$pK_{BH}^{+a}$
$Ph_3SiCOPh$	1.00 <sup>b</sup>		-7.78
$Ph_3GeCOPh$	0.94 <sup>b</sup>	0.86 <sup>c</sup>	— <sup>d</sup>
$Ph_3CCOPh$	0.84 <sup>b</sup>	0.78 <sup>c</sup>	-8.37
$Me_3SiCOPh$	1.00 <sup>b</sup>		-6.49
$Me_3GeCOPh$	0.97 <sup>b</sup>		-6.51
$Me_3CCOPh$	0.90 <sup>b</sup>		-7.74

<sup>a</sup> Dissociation constants of ketone conjugate acids—values are not thermodynamic  $pK$ 's.

<sup>b</sup> From frequency shifts on bonding to phenol.

<sup>c</sup> From frequency shifts on bonding to methanol.

<sup>d</sup> Decomposed.

The data, which are relatively self-consistent regardless of the method, indicate that acylsilanes and acylgermanes are significantly more basic than their carbon analogs for both trimethyl and triphenyl derivatives. In each case, the silicon compound is slightly more basic than the germanium compound.

### B. Ultraviolet Absorption Spectra

The ultraviolet-visible spectral properties of acylmetalloid compounds are particularly interesting. The details for all known compounds are given

in Tables III and IV and a summary of the several bands observed in the spectra of typical fully aliphatic and fully aromatic compounds is given in Table VII. These will be discussed in turn.

TABLE VII  
TYPICAL SPECTRAL DATA FOR ACYLMETALLOIDS

Type of absorption	C	Si	Ge
	Me <sub>3</sub> CCOMe	Me <sub>3</sub> SiCOMe	Et <sub>3</sub> GeCOMe
<i>n</i> - $\pi^*$	278(15)	372(126) <sup>a</sup>	365(173) <sup>a</sup>
<i>b</i>	186(1100)	195(4,200)	<i>c</i>
	Ph <sub>3</sub> CCOPh	Ph <sub>3</sub> SiCOPh	Ph <sub>3</sub> GeCOPh
<i>n</i> - $\pi^*$	329(299)	424(292) <sup>a</sup>	417(210) <sup>a</sup>
$\pi$ - $\pi^*$	251(11,600)	257(16,200)	254(16,200)
<i>d</i>	191(117,000)	195(162,000)	193(56,100)

<sup>a</sup> These absorptions are strongly banded; see Tables III and IV for details.

<sup>b</sup> This may be the  $\pi$ - $\pi^*$  transition but the identity has not been positively established.

<sup>c</sup> Not measured.

<sup>d</sup> The identity of this transition is not known; it may be due to the second primary benzene transition.

All ketones have long-wavelength, low-intensity absorption due to  $n$ - $\pi^*$  excitation of the carbonyl group. With alkyl silyl ketones this occurs near 380 m $\mu$ , some 100 m $\mu$  to longer wavelength than for the corresponding carbon compound pinacolone,  $\lambda_{\max}$  279 m $\mu$ . For aryl silyl and germyl ketones, the  $n$ - $\pi^*$  band is near 420 m $\mu$ , about 90 m $\mu$  to longer wavelength than in  $\beta$ -benzpinacolone,  $\lambda_{\max}$  329 m $\mu$ . In both cases the bathochromic shifts correspond to a lowering in the energy of the  $n$ - $\pi^*$  transition by about 21–26 kcal/mole.

The assignment of these bands as  $n$ - $\pi^*$  is based on the observed progressive blue shift as the solvent is made more polar (9, 44), a phenomenon characteristic of carbonyl  $n$ - $\pi^*$  absorption (45, 46). The intensities of the bands are usually much greater than for the carbon analogs, as, for example, acetyltrimethylsilane,  $\epsilon$ 126 and pinacolone,  $\epsilon$ 21. The absorption band in all cases shows considerable fine structure, usually consisting of three main bands with two additional shoulders at lower wavelengths. The separations

between the bands, which have been mathematically resolved, are of the order of  $1000\text{--}1200\text{ cm}^{-1}$ ; this is consistent with the expected values of C—O vibrational frequencies in the  $n\text{--}\pi^*$  excited state (44). Usually, vibrational structure does not persist in polar solvents, and its survival with the acyl-metalloids is not understood.

Aryl silyl and germyl ketones have an intense absorption band in the region  $250\text{--}260\text{ m}\mu$ . This band is the  $\pi\text{--}\pi^*$  transition of the acyl group ( $\text{Ar}\text{--C=O}$ ) and neither the position nor the extinction coefficient varies greatly, regardless of whether carbon, silicon, or germanium is attached to the carbonyl group:  $\text{Ph}_3\text{SiCOPh}$ ,  $257\text{ m}\mu$  ( $\epsilon 16,200$ );  $\text{Ph}_3\text{GeCOPh}$ ,  $254\text{ m}\mu$  ( $\epsilon 16,200$ );  $\text{Ph}_3\text{CCOPh}$ ,  $251\text{ m}\mu$  ( $\epsilon 11,600$ ). These wavelength differences correspond to differences in the transition energy of about  $2\text{--}3\text{ kcal/mole}$ . These bands undergo slight red shifts as the solvent becomes more polar, as expected for conjugated carbonyl transitions where the transition dipole is towards oxygen. Several other characteristic bands have been observed in certain classes of compounds. Acetyltriphenylmetaloids ( $\text{M} = \text{C}, \text{Si}, \text{Ge}$ ) have characteristic benzenoid B bands of moderate intensity ( $\epsilon 1000\text{--}2000$ ) and considerable fine structure in the  $260\text{--}280\text{ m}\mu$  region—in benzoylmetaloids these bands are largely obscured by the intense  $\pi\text{--}\pi^*$  transition described above.

Tris(*p*-substituted)phenylbenzoylsilanes have an intense absorption in the region of  $220\text{--}230\text{ m}\mu$  ( $\epsilon \sim 40,000$ ), which is possibly the primary benzene band, shifted to longer wavelengths by the *p*-substituents.

Finally all ketones have absorption in the region of  $185\text{--}195\text{ m}\mu$ —with benzoyltriphenylsilane this occurs at  $195\text{ m}\mu$ , and with  $\beta$ -benzopinacolone at  $191\text{ m}\mu$ , an energy difference of about  $7\text{ kcal/mole}$ . With compounds having phenyl groups attached it has been suggested that this is either a primary benzene band, or a second  $\pi\text{--}\pi^*$  type absorption. When only alkyl groups are present, the transition, at  $195\text{ m}\mu$  ( $\epsilon 4200$ ) for acetyltrimethylsilane and  $186\text{ m}\mu$  ( $\epsilon 1100$ ) for pinacolone, may be due to a  $\pi\text{--}\pi^*$  transition of the carbonyl group.

The difference in energy of these transitions is about  $9\text{ kcal/mole}$ , and like the  $\pi\text{--}\pi^*$  transition of the benzoyl compounds, the transition for silicon is of lower energy.

The positions of the  $n\text{--}\pi^*$  and  $\pi\text{--}\pi^*$  bands described above are essentially independent of the type of group attached to the metalloid atom—trimethyl-, triphenyl-, and hydroxydiphenylbenzoylsilanes differ in the position of their bands by no more than  $3\text{--}4\text{ m}\mu$ .

The interpretation of the above data presents several problems, and several different points of view have been advanced. These are considered in Section VI.

### C. Nuclear Magnetic Resonance

Protons attached to a carbon atom adjacent to the carbonyl group of acylsilanes and -germanes are deshielded relative to their carbon analogs. Data illustrating this behavior, which must involve both the effects of electronegativity and magnetic anisotropy, are given in Table VIII.

TABLE VIII  
NUCLEAR MAGNETIC RESONANCE POSITIONS  
OF ACYLMETALLOIDS<sup>a</sup>

Class	M = C	Si	Ge
Me <sub>3</sub> MCOMe	2.07	2.18	2.20 <sup>b</sup>
Ph <sub>3</sub> MCOMe	2.01	2.30	2.38

<sup>a</sup> Positions are given as  $\delta$ , in ppm below TMS, used as internal standard in carbon tetrachloride solution.

<sup>b</sup> Compound was Et<sub>3</sub>GeCOMe.

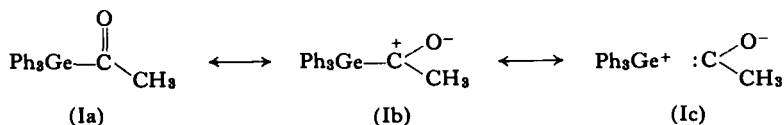
## IV

### THE STRUCTURE OF ACETYLTRIPHENYLGERMANE BY X-RAY DIFFRACTION TECHNIQUES

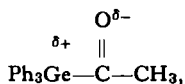
An X-ray diffraction study of the crystal structure of acetyltriphenylgermane has recently been completed (47). In view of the fact that acylsilanes and -germanes have very similar spectral properties, but at times markedly different chemical properties (see below) it is not clear whether the results found are also applicable to acylsilanes. The structure study, carried to a high degree of refinement in which most hydrogen atoms were located, indicated that the three phenyl groups and the acetyl group were located tetrahedrally about the germanium center, the three phenyls being oriented in a slightly unsymmetrical propeller fashion. Whereas the phenyl-Ge bond lengths were  $1.945 \pm 0.008$  Å (found for MeGeH<sub>3</sub> 1.945 Å), the Ge—C (acetyl) bond length was significantly longer at  $2.011 \pm 0.015$  Å. The C=O bond length, which might have been expected to be abnormally



long reflecting the unusually long wavelength carbonyl absorption ( $6.00 \mu$ ), and the enhanced basicity (31), was found to be  $1.20 \pm 0.002 \text{ \AA}$ , actually slightly shorter than the  $1.21_5 \text{ \AA}$  normally found in ketones. The angles involving the carbonyl group were within a degree of the theoretical  $120^\circ$ , and the  $\text{CH}_3\text{—CO}$  bond length of  $1.51 \text{ \AA}$  was normal. Trotter ascribes the lengthening of the  $\text{Ge—C}$  (acetyl) bond to contributions to the structure not only of the species (Ia) and (Ib),



whose carbon analogs contribute to the structure of ordinary ketones, but also (Ic), a structure considered possible because of the considerable difference in electronegativity between germanium and carbon. The molecule is thus written as



which is said to account for the basicity of the ketones found by Yates and Agolini (31), and for the long  $\text{Ge—C}$  (acetyl) bond.

With the long  $\text{Ge—acetyl}$  bond length and the normal  $120^\circ$  bond angle, there is obviously no indication of a shortened  $\text{Ge—O}$  distance, as might have been expected if a direct field or  $\sigma(p\text{—}d)$  bonding between oxygen and germanium were important. Nor is the lengthened  $\text{Ge—acetyl}$  bond consistent with  $\pi(\pi\text{—}d)$  interaction between the carbonyl group and the germanium  $4d$  orbitals in the ground state.

In view of the general evidence that bond lengths of carbonyl compounds increase with increasing polarity (48), and that there is a relationship between bond length and stretching frequency (49), the short length of the carbonyl bond in the acetylgermane is surprising and it will be a matter of some interest to see what value is found for an acylsilane.

## V

### REACTIONS OF ACYLMETALLOIDS

The chemistry of the acylmetaloids is still in an early stage of exploration. Most work has been done on the acylsilanes and the studies completed to

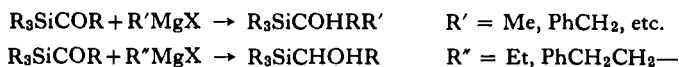
date show that the compounds frequently behave as typical ketones, but abnormal behavior involving rearrangements leading to silicon-oxygen bond formation are exceedingly common, particularly from reactions with nucleophilic reagents. Thus, these rearrangements are special examples of the silylcarbinol to silyl ether rearrangement (30). On the other hand, acylgermanes show no tendency toward rearrangements and, apart from a marked susceptibility toward hydrolysis, behave much like their carbon analogs.

### A. Derivatives

Few simple derivatives of acylsilanes have been described, although a phenylhydrazone has been reported (1) and tosylhydrazones of several ketones have also been prepared (24). Attempts to prepare oximes led to decomposition, almost certainly the result of the sensitivity of the ketones to basic media.

### B. Lithium Aluminum Hydride and Organometallic Reagents

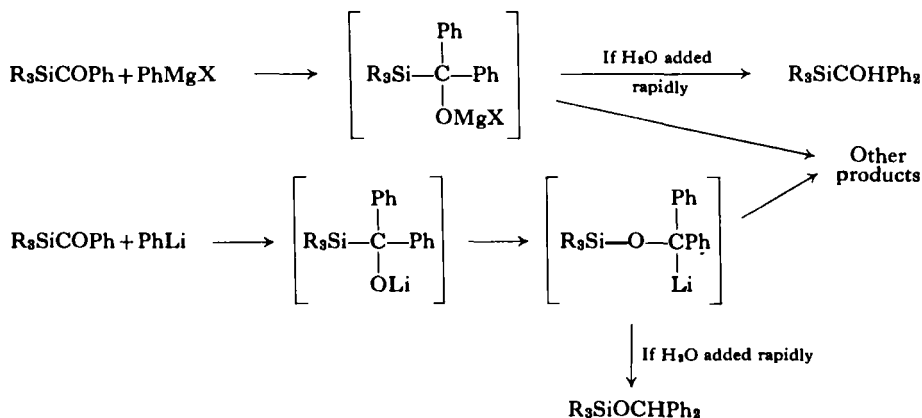
All acylsilanes are smoothly reduced to the corresponding carbinol with lithium aluminum hydride without complications (2, 24, 30). Reactions with organometallic reagents appear to take at least two different courses. With Grignard reagents having no  $\beta$ -hydrogens, e.g., methyl- or benzylmagnesium halide, normal addition to give the expected tertiary alcohol occurs in good yield (2, 30). However, if the Grignard reagent has a  $\beta$ -hydrogen, and hence is capable of reducing the ketone, this reaction predominates and little or no adduct is formed (2).



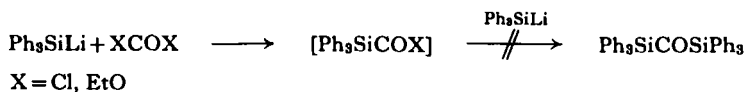
Acylsilanes appear to be extraordinarily susceptible to reductions of this type.

Aryl organometallics, for example phenylmagnesium bromide, add readily to alkyl silyl ketones to give the expected carbinol, but with aryl silyl ketones complex reactions occur. Thus benzoyltriphenylsilane and phenylmagnesium bromide give large yields of triphenylsilanol and benzophenone, and significant quantities of tetraphenylethylene and other material of unknown structure. Studies involving very rapid mixing of reagents and work-up yielded the expected carbinol in moderate yield,

indicating that normal addition to form the carbinol must occur, rapidly followed by other reactions leading to the observed products (19). When phenyllithium was used instead, under similar conditions, low yields of benzhydryloxytriphenylsilane were obtained, indicating clearly that under these conditions normal addition was followed by rapid silylcarbinol to silyl ether rearrangement.



One other related study warrants mention. Attempts to prepare bis(triphenylsilyl) ketone by reaction of triphenylsilyllithium with either phosgene, diethyl carbonate, or ethyl chloroformate failed (50).

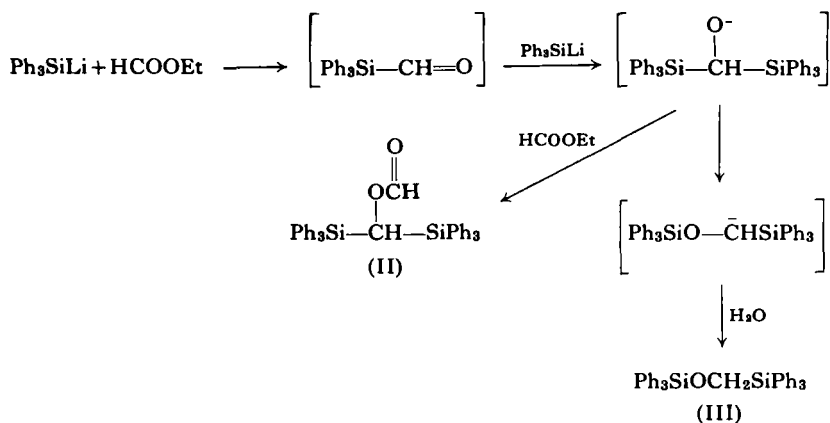


However, when ethyl formate was treated with triphenylsilyllithium, the major products were 1,1-bis(triphenylsilyl)methyl formate (II) (22%), triphenylsiloxy(triphenylsilyl)methane (III) (30%), and triphenylsilanol (41%).

The former evidently arose from trapping by ester interchange of an intermediate silylalkoxide formed by normal addition of silyllithium to triphenylsilylformaldehyde formed *in situ*, whereas the latter (III) is the commonly found rearrangement product of a silylalkoxide ion.

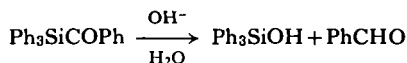
The comparable reaction of triphenylgermyllithium with ethyl formate gave a mixture of bis(triphenylgermyl)carbinol and its formate, but no rearrangement product corresponding to (III) was obtained because of the failure of germylalkoxide ions to rearrange. Incidentally, the above reactions

constitute good experimental evidence for the existence of aldehydosilanes and -germanes. Numerous attempts at direct synthesis by a variety of routes have failed, carbon monoxide and hydrolysis products being formed (see also Sommer *et al.*, 40).

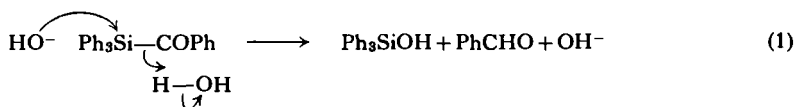


### C. Hydrolysis and Reactions with Alkoxide Ions

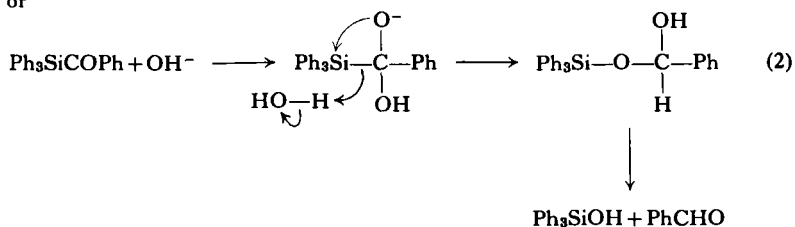
Acylsilanes are highly sensitive to basic media—thus solutions in alcohol of benzoyltriphenylsilane to which a trace of aqueous base is added, rapidly lose their yellow color and yield triphenylsilanol and benzaldehyde (1).



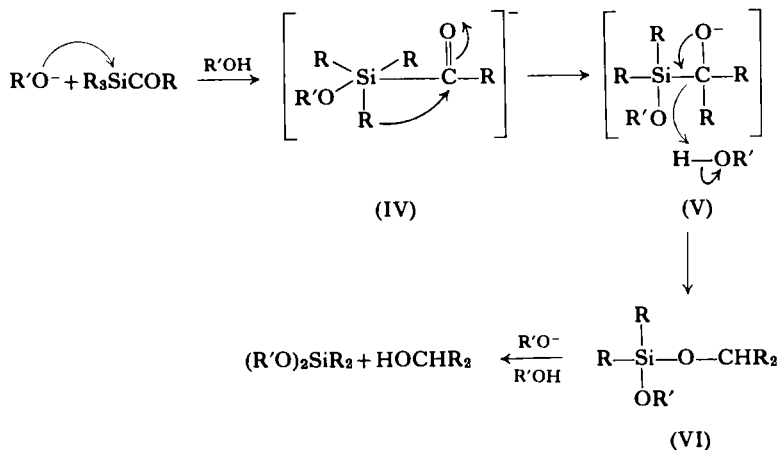
Two mechanisms seem possible for this reaction—nucleophilic attack on silicon [Eq. (1)], or nucleophilic attack on carbon followed by rearrangement [Eq. (2)], to give a hemiacetal which would subsequently decompose.



OF

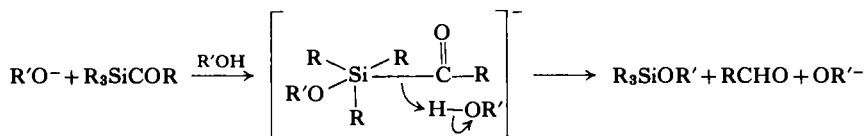


In the hope of clarifying this situation studies were made (3, 51) of the reaction of acylsilanes with alkoxide ions, since the anticipated intermediate in this case, according to Eq. (2), would be a ketal which would be expected to be reasonably stable and hence isolable. Instead a new type of rearrangement was observed, as shown below.

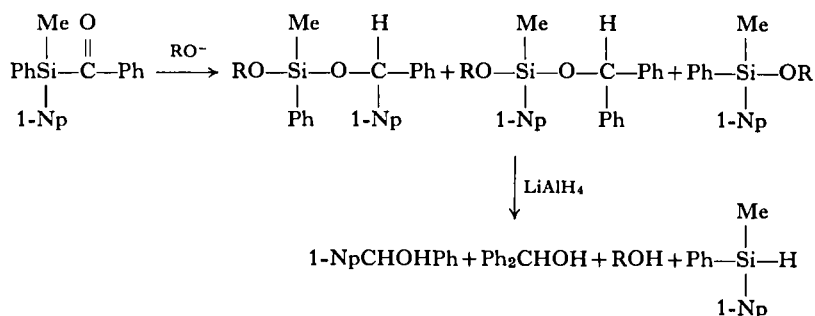


The reaction can be interpreted in terms of nucleophilic attack by alkoxide ion on the silicon atom of the ketone to give an Si (5) pentacoordinate species (IV). This species subsequently undergoes 1,2-migration of an R group (usually aryl, although alkyl migration was observed in the absence of any possible aryl migration) from silicon to the carbonyl carbon atom, yielding the silylalkoxide ion (V). Thus the reaction mechanism to this point closely parallels the benzilic acid rearrangement. The intermediate (V), which was not isolated, then rearranges according to the now well established pathway of the silylcarbinol to silyl ether rearrangement (30, 52) to yield as the major product in most cases the unsymmetrical dialkoxysilane (VI). Other products of the reaction, namely symmetrical dialkoxysilane and carbinol, arise from ether interchange between the unsymmetrical dialkoxysilane and the alkoxide ion present. Whether the species (IV) is a transition state or an intermediate cannot be established from the available data.

A second competing reaction, direct displacement of the acyl group from silicon, invariably accompanies the above rearrangement. This simple displacement reaction appears to be favored over rearrangement as the solvent system becomes more polar (3).



Stereochemical studies (26) of the reaction using (+)-1-naphthylphenylmethylbenzoylsilane showed that the displacement part of the reaction (13%) occurred with at least 90% stereospecificity and involved retention of configuration at silicon,



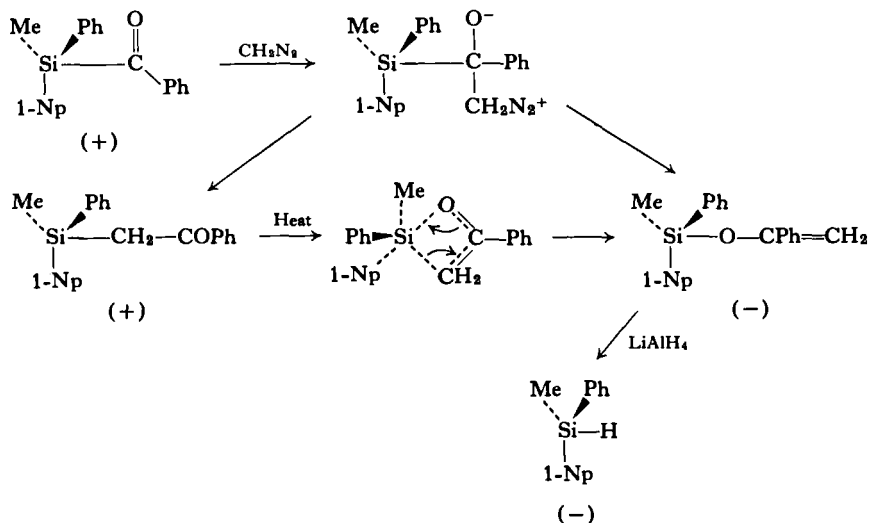
since reduction of the resulting alkoxy silane with lithium aluminum hydride, a reaction known to occur with retention of configuration (53, 54) gave (–)-1-naphthylphenylmethylsilane. The rearrangement part of the reaction (at least 60%), also could be studied stereochemically. Since either phenyl or naphthyl groups migrated from silicon to carbon (the ratio of phenyl to naphthyl migration was 3.6:1) a complex mixture of products was obtained which on reduction with lithium aluminum hydride gave a separable mixture of silanes and carbinols. Of these, 1-naphthylphenylcarbinol, resulting from 1-naphthyl migration, was found to be optically active, indicating that the rearrangement part of the reaction also occurred with some stereoselectivity.

#### D. Diazomethane and Alkylidenephosphoranes

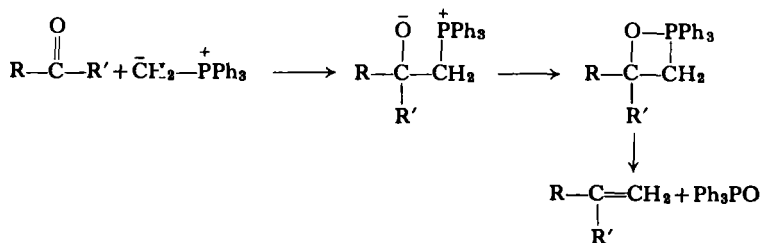
The reaction of ketones with diazomethane has been thoroughly studied (55); homologous ketones or epoxides are the usual reaction products. With acylmetalloids two alternative ketones could be formed, depending on whether the silyl (or germyl) group or the (R') group attached to the carbonyl underwent the 1,2-migration.



naphthylphenylmethylsilyl)acetophenone also arose from (+)-1-naphthylphenylmethylbenzoylsilane with retention of configuration. This finding is consistent with the known stereochemistry of ketone homologation using diazomethane (58, 59).

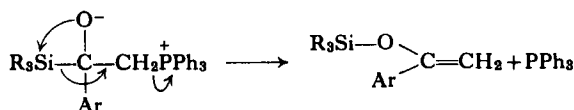
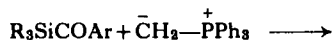


The normal products from the reaction of a ketone with an alkylidene-phosphorane (Wittig reagent) are an alkene and a phosphine oxide (60). This reaction has been investigated with acylmetaloids, and in view of the fact that both the Wittig reagent and diazoalkanes have important resonance

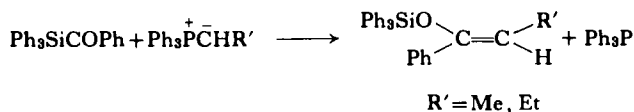


contributors in which negative charge is localized on the methylene group, it seemed likely that the behavior of acylmetaloids with alkylidenephosphoranes might parallel their behavior with diazomethane. In fact with a variety of aryl silyl ketones none of the expected alkenes were obtained and the reaction products were found to be siloxyalkene and triphenylphosphine (11).



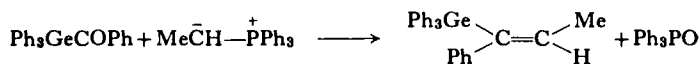
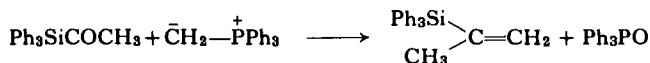


Similar products were obtained with alkyl-substituted methylenephosphoranes and only a single geometric isomer, the *trans*-alkenylbenzene derivative was obtained.



As with the analogous diazomethane case, the reaction can be interpreted as an intramolecular nucleophilic attack on silicon by the electron-rich oxygen of the original carbonyl group, leading to silicon-carbon bond cleavage, formation of the alkene double bond, and loss of triphenylphosphine.

On the other hand, with alkyl silyl ketones or with acylgermanes, only the normal Wittig products, alkene and phosphine oxide, were obtained in good yield.

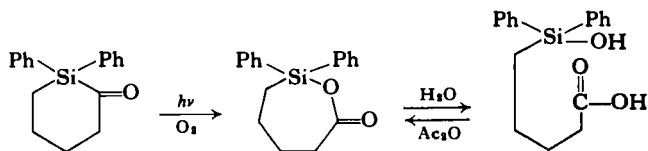


Hence the direction which the reaction takes depends strongly both on the nature of the organic group attached directly to the carbonyl group (alkyl or aryl) and on the nature of the metalloid atom also directly attached (Si or Ge).

### E. Photochemistry

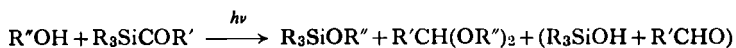
During the preparation and attempted isolation of 1,1-diphenylsilacyclohexanone-2 it was observed that material believed to be the ketone was unstable in light, particularly in the presence of air (61). Investigation indicated that the ketone, which has  $n-\pi^*$  carbonyl absorption in the region

370–390  $m\mu$ , was undergoing photooxidation promoted by the room illumination, to a cyclic lactone. The lactone subsequently hydrolyzed to a  $\delta$ -(hydroxysilyl)carboxylic acid of known structure (20), and could be reconstituted from the acid by refluxing in acetic anhydride. The ketone was stable in the dark in the presence of oxygen over long periods of time.

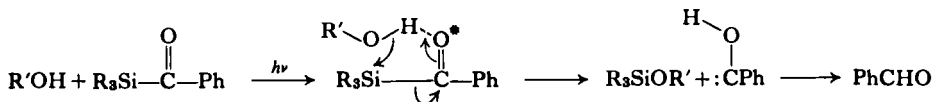


Subsequent work showed that this reaction was common to other alkyl silyl ketones such as acetyltriethylsilane, which gave acetoxypentamethylsilane, but that aryl silyl ketones such as the benzoylsilanes were inert toward photochemical oxidation.

Alcoholic solutions of acylsilanes also react with dramatic ease and speed in the presence of near-visible radiation (62). In systems employing only purified alcohol, or those to which traces of acid have been added, the main reaction process appears to involve displacement of the acyl group from silicon to yield a silyl ether and an acetal together with small, but variable, amounts of silanol and free aldehyde.



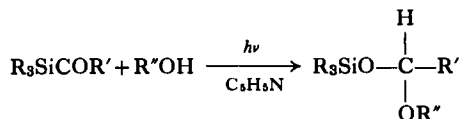
This type of reaction was also reported by Kuivila (63). Using optically active (+)-1-naphthylphenylmethylbenzoylsilane the reaction gave (–)-1-naphthylphenylmethylmethoxysilane corresponding to 78% net retention of configuration. It would seem reasonable for this reaction to occur by reaction of excited ketone (protonated?) with hydrogen-bonded alcohol, the cyclic concerted mechanism leading to retention of configuration.



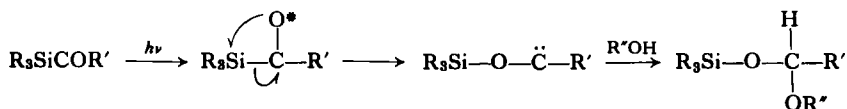
Similar pathways have been proposed to account for the behavior of  $\alpha$ -ketocarboxylic acids (64).

Distinct from the above behavior which occurs in “neutral” or acidified alcohol, is the almost quantitative formation of the mixed acetal of the

aldehyde with silanol and solvent which occurs when an alcoholic solution of an acylsilane containing trace amounts of base, particularly pyridine, is photolyzed.

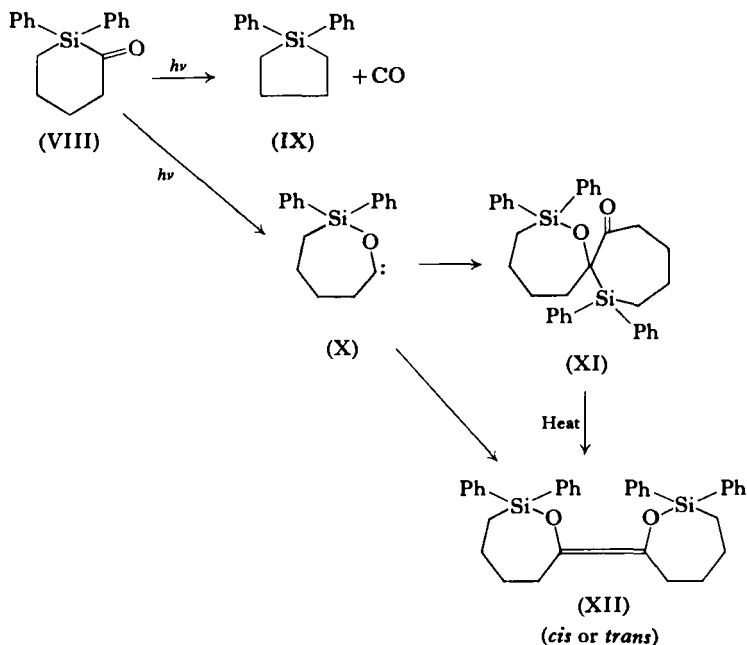


This appears to be a general reaction for both acyclic and cyclic ketones (17) and other protic reagents besides alcohols, such as amines and HCN, give comparable products (19). It is considered that these products arise through the photochemical generation from the acylsilane of a siloxycarbene, which subsequently inserts into the alcoholic O—H bond.



As frequently noted before, the formation of the silicon-oxygen bond occurs here also with virtually complete retention of configuration based on studies with (+)-1-naphthylphenylmethylbenzoylsilane. Similar photochemical formation of oxacarbenes have recently been reported by several workers (65-68). The role of base and acid in leading to these apparently unrelated pathways is not yet understood. Qualitative rate studies indicate that conversion of the mixed acetal to the alkoxysilane and acetal under comparable acid conditions is much slower than their direct photochemical formation so that the mixed acetal does not appear to be an intermediate in the reactions containing acid.

Photolyses of cyclic and acyclic acylsilanes in inert solvent media also occur readily. For example, 1,1-diphenylsilacyclohexanone (VIII) (17, 61) has been shown to undergo photolysis in cyclohexane, yielding significant quantities of the Norrish Type I decarbonylation product diphenylsilacyclopentane, (IX). In addition, two photodimers, (XI) and (XII), are found which are believed to have the structures shown; the first of these (XI) is thermally convertible into the second. The  $\beta$ -ketosilane-siloxyalkene transformation required in this thermal rearrangement has recently been found to be a general reaction (57). The formation of these dimers is presumed to proceed through the siloxycarbene, (X).

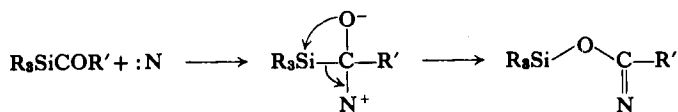


There is some evidence that acylgermanes may behave like their silicon analogs, but the reactions have not been extensively investigated as yet (19).

### F. Summary of Reactions

The preceding data on the reactions of acylmetalloids indicate two general types of behavior. On the one hand the compounds may show behavior typical of a normal (carbon) ketone. This is particularly true of acylgermanes, as exemplified by their behavior with diazomethane, methylenetriphenylphosphorane, and photochemically. Alkyl silyl ketones ( $\text{R}_3\text{SiCOAlk}$ ) also frequently show normal behavior, as with organometallic reagents, diazomethane, and alkylidenephosphanes, although unusual photochemical behavior was observed. On the other hand with virtually all reagents employed, at least part, if not all, of the reaction products derived from aryl silyl ketones ( $\text{R}_3\text{SiCOAr}$ ) were "abnormal" products, which arose from reaction pathways unknown to carbon ketones. The majority of these abnormal reaction products can be interpreted as arising from the single reaction mechanism shown below, in which a

nucleophile  $\text{N:}$  attacks the carbon of the carbonyl group, changing the hybridization from  $sp^2$  to  $sp^3$ , and forming an alkoxide ion.



In the succeeding step, attack on silicon by the alkoxide oxygen leads to cleavage of the silicon-carbon bond and usually multiple bonding between carbon and N. This second step in the reaction is thus closely related to the silylcarbinol to silyl ether rearrangement. In both reactions, it is the nature of the group  $\text{R}'$  which appears to govern the facility of the reaction. When  $\text{R}'$  is aromatic, and thus capable of stabilizing incipient carbanion formation as the silicon-carbon bond cleaves, the reaction occurs readily, and much, if not exclusive, silyl ether type product is found. If  $\text{R}'$  is alkyl, and hence carbanion-destabilizing, the rearrangement is inhibited and generally does not occur at all, or at best, is very slow relative to the alternative "normal" reaction pathway. Where rearrangement occurs, a considerable body of evidence indicates that the configuration of an asymmetric silicon center is retained with a high degree of stereospecificity.

It would seem likely that any  $p$ - $d$  interaction between the charge on oxygen and the  $d$  orbitals in the metalloid would also facilitate the rearrangement by lowering the energy of activation. If this is so, then the fact that acylgermanes completely fail to show any evidence at all for rearrangement must imply that  $p$ - $d$  interaction using  $4d$  orbitals does not occur to the same extent as with the  $3d$  orbitals on silicon.

## VI

### DISCUSSION OF ACYLMETALLOIDS

The foregoing has attempted to indicate the extent of our knowledge concerning the properties of acylmetalloids. It is quite clear that the underlying reasons for some of the observed differences in behavior of the carbonyl compounds of silicon and germanium are not well understood.

The salient points may be summarized as follows:

(a) Acylsilanes and acylgermanes have very similar infrared and ultra-violet spectra, the  $\lambda_{\text{max}}$  of which occur at much longer wavelengths than in

their carbon analogs. The nature of the spectra is little influenced by the nature of the groups attached to the metalloid atom.

(b) Considerable differences in chemical behavior exist between acylsilanes and acylgermanes, the former having a strong tendency to undergo unique rearrangements which involve silicon-oxygen bond formation and silicon-carbon bond cleavage. Under similar or more severe conditions, the germanium compounds have never been observed to rearrange, and in fact, in their chemical behavior they closely resemble their carbon analogs.

(c) Acylsilanes, and to a slightly lesser extent acylgermanes, are significantly stronger bases than their carbon counterparts. This order of basicity closely parallels the expected electron density on the carbonyl group caused by electron release from the metalloid atoms due to their low electronegativity compared to carbon.

The differences in behavior of silicon and germanium compounds on the one hand and carbon compounds on the other, are frequently explained as being due primarily to  $\pi$ -bonding between the empty  $d$  orbitals of the metalloid and either unshared pairs of electrons in  $p$ -type orbitals,  $\pi(p-d)$  bonding, or  $\pi$ -type orbitals,  $\pi(\pi-d)$  bonding, located on an adjacent functional group. The evidence for  $\pi(p-d)$  bonding in silanols, silyl ethers, and disiloxanes is reasonably compelling (69, 70) but the situation pertaining when nitrogen is the atom adjacent to the metalloid atom is in dispute (71, 72).

When a carbonyl group is the adjacent functional group, one can conceive of  $d$ -orbital interaction with the carbonyl  $\pi$ -system,  $\pi(\pi-d)$  bonding, or of "1-3" or "across space" interaction with the unshared electrons on the oxygen of the carbonyl group,  $\sigma(p-d)$  bonding, or both.

Several suggestions have appeared at various times, attempting to explain the preceding data. It was originally suggested that the spectral data of acylsilanes might be explained if the electron-rich oxygen of the polarized carbonyl group interacted with the energetically available  $3d$  orbitals on silicon (2), a situation which ought to stabilize the molecule. This type of interaction implies  $\sigma(p-d)$  bonding or a field effect, although the term  $d\pi-p\pi$  bonding was originally used.

Inductive effects, due to the lower electronegativity of silicon and germanium relative to carbon were later recognized as satisfactorily explaining the successive shift to lower wavelengths of the carbonyl stretch in acyl-,  $\beta$ -keto-, and  $\gamma$ -ketometalloids (10) (see Section III,A).

In 1963 Orgel (73) pointed out that a triorganosilyl group acting as both  $\sigma$ -donor and  $\pi$ -acceptor could stabilize the  $\pi$ - $\pi^*$  excited state of a ketone relative to its ground state, and suggested that this might account for the unusual spectra of acylsilanes. Similar suggestions were independently put forward by West (74, 75), who emphasized the  $\pi$ -bonding aspect, inferring, as shown in Fig. 1, that while inductive effects of the metalloid

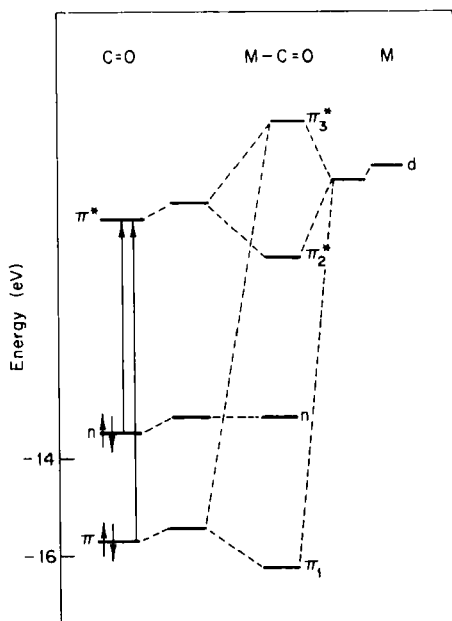


FIG. 1. Orbital energy diagram for acylmetaloids according to West (75).

atom would raise all three energy levels ( $n$ ,  $\pi$ ,  $\pi^*$ ) slightly, the major effects would come from interaction of these orbitals with the metalloid  $d$  orbitals. Thus the energy levels of the unshared ( $n$ ) electrons on oxygen were considered to be relatively unaffected because of their remoteness from the silicon atom, but resonance interaction between the  $d$  orbitals and the  $\pi^*$ -orbital particularly (because of better energy matching) would result in significant lowering of the  $\pi^*(\pi_2^*)$  orbital relative to the  $n$  level. Thus the stabilization would involve the excited state primarily. A consequence of this argument is that the  $\pi$ -orbital should not be greatly lowered in energy in the resonance system because of poorer energy matching between the  $\pi$ -orbital and  $d$  orbital.

These explanations nicely account for the observed longer wavelength of the  $n\text{-}\pi^*$  transition of 80–100  $m\mu$  (21–26 kcal/mole). However, they inevitably predict a similar shift to longer wavelength of the  $\pi\text{-}\pi^*$  transition if the  $\pi^*$  level is lowered but the  $\pi$  remains at about the same level, whereas in fact only minor shifts of 3–10  $m\mu$  (2–8 kcal/mole) are observed. West's calculations (75) indicated that in a silylalkene the  $\pi^*$  and  $d$  energy levels

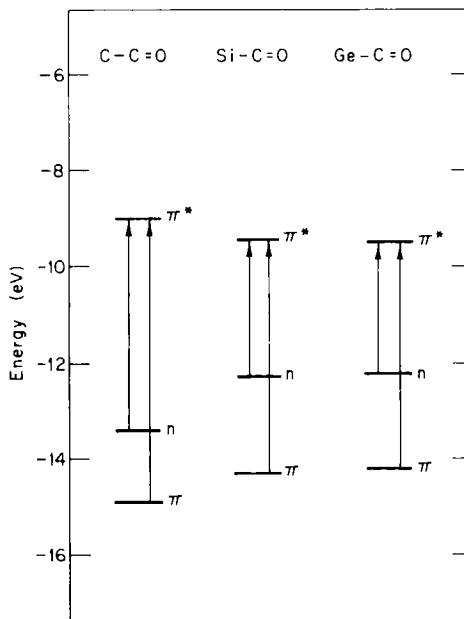


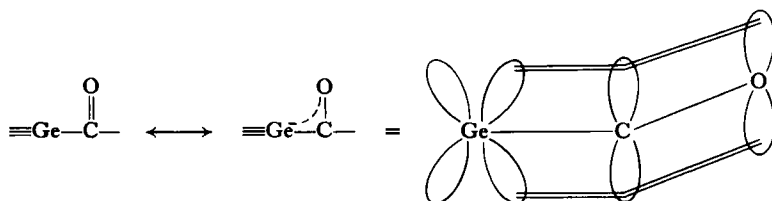
FIG. 2. Orbital energies from extended HMO calculations of Yates (44) (same scale as Fig. 1).

of the double bond and silicon atom, respectively, were reasonably closely matched ( $\sim 0.8$  eV) and hence resonant interaction of the  $\pi^*$  and  $d$  orbitals seemed energetically favorable. The same sort of calculations for a silicon-carbonyl system, where the ionization potential of a ketone ( $\sim 9.7$  eV) involves removal of an  $n$  electron (14), indicate an energy difference of about 3.4 eV between the  $\pi^*$  and  $d$  orbitals, so that the energies of the two orbitals are in fact not comparable and significant interaction would not be expected.

If  $\pi\text{-}d$  bonding is the chief means of lowering the transition energy between the  $n$  and  $\pi^*$  state in acylmetalloids by the observed 21–26 kcal/mole, then it is impossible to avoid recognizing that considerable  $\pi$ -bonding must



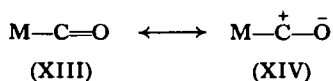
exist in the ground state as well, since the  $\pi-\pi^*$  transition energy remains relatively constant (to within 2–3 kcal/mole for benzoylmetalloids and 7–8 kcal/mole for acylmetalloids bearing only alkyl groups) for the carbon-, silicon-, and germanium-containing ketones. While direct evidence for or against  $\pi$ -bonding in the excited state is difficult to obtain, there is evidence regarding the situation in the ground state. Thus contributions from structures such as those below might have been expected to shorten the Ge—C (acetyl) bond in acetyltriphenylgermane, whereas in fact it is found to be abnormally long (47).



Such contributions would also be expected to reduce the electron density of the carbonyl oxygen relative to molecules where such  $\pi$ -bonding did not exist, yet acylsilanes and -germanes are in fact observed to be markedly stronger bases than their carbon analogs (31). Also  $\pi$ -bonding would be expected to raise the carbonyl stretching force constant of these compounds, but in fact their carbonyl absorption occurs at remarkably long wavelength, indicating a reduced force constant.

On the other hand, inductive effects, due to the large electronegativity difference between silicon (or germanium) and carbon, will account reasonably well for many of the observed phenomena. Inductive release will of course raise the  $n$  energy level, thereby reducing the  $n-\pi^*$  transition energy while not significantly affecting the  $\pi-\pi^*$  transition. In this connection it is worth noting that the lowering of the  $n-\pi^*$  transition energy in the bis(silyl) ketones (50 kcal/mole) is about twice that observed for acylsilanes (16) so that the effects of adjacent metalloid atoms appear additive.

Inductive release from the metalloid atom toward the carbonyl group should also favor polarization of the carbonyl group and structure (XIV) would be expected to be a significant contributor, as is indicated by the



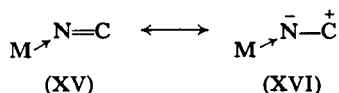
longer wavelength infrared absorption and higher basicity of acylsilanes and acylgermanes, compared with carbon ketones. However, it would not have been anticipated that the carbonyl group of acetyltriphenylgermane would be as short as the 1.20 Å reported by Trotter (47), although the available data on bond length-stretching frequency correlations (49) do show considerable variations in stretching frequencies for compounds with carbonyl bond lengths in the range  $1.20 \pm 0.02$  Å.

The recent paper of Rochow on the spectral properties of *N*-metalloidal ketimines,  $R_3M-N=CR_2$  where  $M = C, Si, Ge, Sn, Pb$  is of some interest (76). These compounds, like the acylmetalloids, show both  $n-\pi^*$  and  $\pi-\pi^*$  transitions in the ultraviolet region; some pertinent data are summarized in Table IX.

TABLE IX  
INFRARED AND ULTRAVIOLET DATA FOR KETIMINES

Compound	Infrared (C=N)		Ultraviolet	
	( $\mu$ )	( $cm^{-1}$ )	$n-\pi^*$	$\pi-\pi^*$
$Ph_3C=NCPH_3$	6.17	1621	305(s)(327)	252( $1.96 \times 10^4$ )
$Ph_3C=NSiPh_3$	6.02	1662	366(157)	259( $2.38 \times 10^4$ )
$Ph_3C=NGePh_3$	6.12	1633	347(125)	255( $1.98 \times 10^4$ )
$Ph_3C=NSiMe_3$	6.09	1642	364(78)	243( $1.63 \times 10^4$ )
$Ph_3C=NGeMe_3$	6.13	1630	347(87)	243( $1.59 \times 10^4$ )

Although the wavelength alters erratically from metalloid to metalloid, the general trend to shorter wavelengths in the infrared data for the C=N linkage as carbon is replaced by silicon, germanium, and tin indicates that the polarized form (XVI) of the linkage is a less important contributor to the structure in these latter cases. This effect would be expected since the



direction of polarization opposes the inductive release of charge from the less electronegative metalloid atoms.

The ultraviolet data for the metalloid ketimines are strikingly similar to those observed for the acylmetalloids, in that regardless of the metalloid

present, the wavelength of the  $\pi-\pi^*$  transition is practically invariant, whereas there is a large bathochromic shift for the  $n-\pi^*$  transition on changing from carbon to silicon, and a slightly smaller one on going from carbon to germanium. The authors consider the possible effects of inductive release, and of both  $\pi(\pi-d)$  and  $\pi(p-d)$  bonding, and conclude that while all these effects may be present, multiple bonding between silicon (or other metalloids?) and the nitrogen atom is small. Thus, the metalloid ketimines obviously behave very similarly to the acylmetalloids, and it appears probable that similar electronic effects govern the behavior of both classes of compound.

In an attempt to investigate the effect of  $\pi$ -bonding in acylsilanes, compounds were synthesized where one of the groups attached to silicon was expected to undergo strong  $\pi(p-d)$  bonding with silicon, presumably at the expense of any possible  $\pi$ -bonding with the carbonyl group (21). These compounds, which had either a hydroxyl or methoxyl group attached to silicon, were found to have infrared and ultraviolet visible spectra virtually identical with those of benzoyldiphenylmethylsilane as reference compound. It was obvious that this additional  $\pi(p-d)$  bonding, if it existed, failed to affect the silicon-carbonyl system significantly, but whether this was because silicon could  $\pi$ -bond to both the carbonyl group and the oxygen simultaneously, which seems unlikely, or whether this implied that no significant  $\pi$ -bonding between silicon and the carbonyl group existed, could not be established from this study. The significance of the spectroscopic data for the bis(benzoyl)silanes (21) is similarly unclear.

In an effort to establish the relative importance of inductive and  $\pi$ -bonding effects ( $\pi^*$ -lowering) in explaining the spectra of acylmetalloids, Yates (44) carried out both simple and extended Hückel molecular orbital calculations, leading to values of the energies of the  $\pi$ -,  $n$ -, and  $\pi^*$ -orbitals for model carbon-, silicon-, and germanium-containing ketones. The calculated results are in remarkably good agreement with the observed transition energies. The results for the system  $H_3MCOMe$  are schematically presented in Fig. 2 (p. 133), which is drawn on the same scale as Fig. 1. Specifically the results show that relative to the carbon model compound, the  $\pi^*$ -level in both acylsilanes and -germanes is somewhat lowered but that the  $n$  level in these latter ketones is raised by about twice this amount above the  $n$  level in the corresponding carbon model. Furthermore, neither the orbital energies nor the total energies calculated for the model compounds were significantly affected by the inclusion or exclusion of  $d$ -orbital parameters

in the calculations. The results suggest then that while a metalloid atom adjacent to a carbonyl group lowers the  $\pi^*$ -energy level, the raising of the  $\pi$  level by the inductive effect of the relatively electropositive metalloid atom is a much more important effect.

To further evaluate possible  $\pi$ -bonding between silicon and the carbonyl group acetylpentaphenyldisilane ( $\text{Ph}_3\text{SiSiPh}_2\text{COMe}$ ) and benzoylpentaphenyldisilane ( $\text{Ph}_3\text{SiSiPh}_2\text{COPh}$ ) were synthesized (77). Numerous studies have shown that the silicon-silicon bond has many of the properties of the carbon-carbon double bond. Thus it undergoes electrophilic attack by perbenzoic acid to give the disiloxane, and electrophilic cleavage by bromine (78). Ultraviolet studies of permethylpolysilanes by Gilman (79) and Kumada (80) have clearly indicated that some kind of delocalized orbital embraces the catenated silicon system, as has also been shown by West in his ESR studies of the anion radicals formed from dodecamethylcyclohexasilane (81). West's studies of *cis*- and *trans*-1,2-bis(trimethylsilyl)-ethene (82, 82a) ( $\text{Me}_3\text{SiCH}=\text{CHSiMe}_3$ ) also indicated delocalization of electrons and hence conjugation throughout the carbon-carbon  $\pi$ -double bond-silicon *d*-orbital system. Similar evidence of such conjugation is also seen in the longer wavelength ultraviolet spectra of vinylsilanes ( $\text{CH}_2=\text{CH}-\text{SiMe}_2\text{SiMe}_3$ ,  $\lambda_{\text{max}}$  223,  $\epsilon$ 5200) compared with vinylsilanes ( $\text{CH}_2=\text{CHSiMe}_3$ ,  $\lambda_{\text{max}}$  202,  $\epsilon$ 1470) (77). With this as background evidence it would have been anticipated, if  $\pi$ -bonding between the carbonyl group and silicon existed, that the absorption spectra of the acyldisilanes would differ from those of the related acylsilanes. In fact no change is observed:  $\text{Ph}_5\text{Si}_2\text{COMe}$ , IR 6.09  $\mu$ ,  $\lambda_{\text{max}}$  245 (27,900), 378 (490);  $\text{Ph}_5\text{Si}_2\text{COPh}$ , IR 6.19  $\mu$ ,  $\lambda_{\text{max}}$  244 (48,000), 423 (342). Further details will be found in Table III. Both the infrared carbonyl stretching wavelength and the  $\pi-\pi^*$  carbonyl transition are virtually unchanged from their monosilyl analogs. The new band at 245  $m\mu$  is, in the case of the acetyl compound, the strong pentaphenyldisilanyl absorption previously observed (83),  $\text{Ph}_6\text{Si}_2$ ,  $\lambda_{\text{max}}$  246.5  $m\mu$  ( $\epsilon$ 32,600), whereas in the benzoyl compound the extinction coefficient indicates this to be the sum of the usual benzoyl  $\pi-\pi^*$  transition band ( $\lambda_{\text{max}}$  257,  $\epsilon$ 16,300) and the pentaphenyldisilanyl absorption band.

Thus, although there is good evidence for  $\pi(\pi-d)$  bonding between silicon and a carbon-carbon double bond, again no evidence is found for  $\pi(\pi-d)$  interaction between silicon and a carbonyl group.

Further evidence for the relative lack of  $\pi(\pi-d)$  bonding between silicon and an adjacent carbonyl group has recently been found by West (84).

In contrast to the observed complete delocalization throughout the molecule of the unshared electron in the anion radical of bis(trimethylsilyl)ethene, the ESR spectrum of the anion radical (ketyl) of acetyltrimethylsilane showed electron delocalization only through the methyl group, with little or no interaction through the silicon  $d$  orbitals involving the protons of the trimethylsilyl group. The ESR spectrum of the anion radical of isobutyryltrimethylsilane similarly indicated little participation of silicon  $d$  orbitals. This further supports the arguments of Brook (10), Yates (44), and Brook and Yates (85) that inductive effects are of primary importance in determining the spectroscopic properties of the acylsilanes.

In summary, a variety of experiments have been carried out in which the effects of  $\pi(\pi-d)$  bonding should have been observable if this kind of interaction was of primary importance in governing the properties of acylmetaloids. In no case was unambiguous evidence found in support of the position that  $\pi$ -bonding plays a major role. Indeed, all of the experimental evidence obtained to date is consistent with the view that the inductive effect, due to release of electron density by the metalloid atom, is dominant in determining the properties of the acylmetaloids.

One further observation merits discussion. The intensities of the  $n-\pi^*$  transitions of acylsilanes and -germanes are in general greater than in the analogous carbon compounds. The  $n-\pi^*$  transition is theoretically forbidden, at least on grounds of local symmetry, because of the orthogonality, and hence lack of overlap, of the two orbitals, and usually the extinction coefficient for such transitions is very low ( $\epsilon 10-20$  for alkyl ketones). The "forbiddenness" is reduced in  $\alpha,\beta$ -unsaturated (conjugated) systems, and in compounds having  $\beta,\gamma$ -unsaturation (i.e., by homoconjugative effects), because of perturbation of the  $n$ -orbital symmetry through overlap and mixing of the  $n$  orbital with the  $\pi$ -system (86, 87).

In the benzoyltriphenylmethanes, -silanes, and -germanes, the extinction coefficients are in fact comparable, probably due to the presence of conjugative and homoconjugative effects in each system. However, with the fully alkylated systems, e.g., acetyltrimethylsilane, acetyltriethylgermane, and pinacolone, the extinction coefficients of the former two are several times that of the latter. This suggests some perturbation of the symmetry of the  $n$  orbitals, perhaps by overlap with the  $d$  orbitals of the metalloid atom, but the effect admittedly is rather small, and it is not clear to what extent overlap need occur to produce effects of the observed magnitude. It is to be noted, as discussed in Section VIII,B, that  $\beta$ -ketosilanes also show enhanced

extinction coefficients relative to their carbon analogs. This phenomenon has been attributed to a direct  $p$ - $d$  orbital interaction (42). These compounds, however, have normal carbonyl ultraviolet absorption wavelengths, although the infrared absorption occurs at longer wavelengths than for the carbon analogs (10, 43).

Finally, attention must be drawn again to the tendency of acylsilanes (and  $\alpha$ -hydroxysilanes) in their chemical reactions to undergo rearrangements leading to silicon-oxygen bond formation and silicon-carbon bond cleavage. The facility with which this occurs can sensibly be attributed to overlap between the lone pairs of the alkoxide oxygen (formerly the carbonyl oxygen) and the silicon  $3d$  orbitals, i.e., "1,3-( $p$ - $d$ ) bonding." While acylgermanes have spectral properties very similar to those of their silicon analogs, neither they (nor  $\alpha$ -hydroxygermanes) show any tendency whatsoever to undergo a similar type of rearrangement leading to germyl ethers. Evidently the  $4d$  orbitals are unable to play a comparable role to the silicon  $3d$  orbitals in facilitating this type of reaction. While one cannot say with certainty that the ability of  $3d$  and  $4d$  orbitals to affect chemical and other changes in behavior at an adjacent  $sp^3$ -hybridized C—O linkage would carry over when the carbon is  $sp^2$ -hybridized as in the acylmetalloids, it does seem possible that these  $d$  orbitals cannot play a dominant role in governing the spectral properties of the ketones, or else acylsilanes and acylgermanes would not be so similar in their physical, and particularly spectral, properties, and so different in their chemical behavior.

## VII

### BIS(SILYL) AND BIS(GERMYL) KETONES

Bis(metalloidal) ketones, compounds having a carbonyl group attached directly to two metalloid atoms ( $\equiv M-CO-M \equiv$ ), have been synthesized by oxidation of the corresponding carbinol, formed by reaction of the silyllithium or germyllithium reagent with ethyl formate (see Section V,B). Bis(triphenylsilyl) ketone (16), bis(diphenylmethylsilyl) ketone (50), and bis(triphenylgermyl) ketone (50) have been made in this way. The compounds known are listed in Table X. In addition, by hydrolysis of 2,2-bis(trialkylmetalloidal)-1,3-dithianes, colored solutions are obtained which have been shown spectroscopically to contain bis(trialkylmetalloidal) ketones. Among those which have been prepared are bis(trimethylsilyl)

ketone (18, 50), bis(triethylgermyl) ketone (7), and trimethylsilyl triethylgermyl ketone (7).

All of these ketones are relatively unstable, and except for the triaryl-metalloid compounds, they have been characterized by spectroscopy only. The spectroscopic data of the known compounds will be found in Table XI. All compounds absorb far into the visible region—for example, bis(triethylgermyl) ketone absorbs at  $\lambda_{\max}$  464, 495, 527  $m\mu$  and bis(triphenylsilyl) ketone at 478, 524, 554  $m\mu$ . The extinction coefficients are not known because of the instability of solutions of the compounds, although the aryl-substituted compounds are quite stable in the solid state in the dark

TABLE X  
BIS(METALLOIDAL) KETONES

Empirical formula	Compound	M.p. (°C)	Method of preparation <sup>a</sup>	References
C <sub>7</sub> H <sub>18</sub> OSi <sub>2</sub>	Me <sub>3</sub> SiCOSiMe <sub>3</sub>	<i>b</i>	C, D	5, 50
C <sub>10</sub> H <sub>24</sub> GeOSi	Et <sub>3</sub> GeCOSiMe <sub>3</sub>	<i>b</i>	D	7
C <sub>13</sub> H <sub>30</sub> Ge <sub>2</sub> O	Et <sub>3</sub> GeCOGeEt <sub>3</sub>	<i>b</i>	D	7
C <sub>23</sub> H <sub>24</sub> OSi <sub>2</sub>	Me <sub>3</sub> SiCOSiPh <sub>3</sub>	<i>b</i>	D	50
C <sub>27</sub> H <sub>28</sub> OSi <sub>2</sub>	Ph <sub>2</sub> MeSiCOSiMePh <sub>2</sub>	<i>b</i>	B	50
C <sub>37</sub> H <sub>30</sub> Ge <sub>2</sub> O	Ph <sub>3</sub> GeCOGePh <sub>3</sub>	152°	C	16, 25
C <sub>37</sub> H <sub>30</sub> OSi <sub>2</sub>	Ph <sub>3</sub> SiCOSiPh <sub>3</sub>	155°–158°	B, C, E	16, 50

<sup>a</sup> Methods of preparation: B, chromic acid oxidation of carbinol; C, oxidation with reagent containing dimethyl sulfoxide; D, hydrolysis of 1,3-dithiane; E, oxidation of carbinol with NBS.

<sup>b</sup> Not isolated.

and in the absence of air. The above wavelengths correspond to transition energies of about 53 kcal/mole for the bis(silyl) ketone. Since the transition energy for acetone is 103 kcal/mole and that for acetyltriphenylsilane is 77 kcal/mole, it is clear that both silicon atoms are similarly affecting the  $n-\pi^*$  transition energy of the intervening carbonyl group.

Little investigation has been made of the reactions of these compounds because of the relative difficulty of their synthesis and their instability, and most of the available studies which have been made have involved bis(triphenylgermyl) ketone.

Reactions with metallic reagents appear to proceed normally; bis(triphenylsilyl) ketone reacted with methyl Grignard reagent to yield the

TABLE XI  
SPECTRAL PROPERTIES OF BIS(METALLOIDAL) KETONES

Empirical formula	Compound	Infrared <sup>a</sup> C=O		Solvent	Ultraviolet
		( $\mu$ )	( $\text{cm}^{-1}$ )		$\lambda_{\text{max}}(\epsilon)$
C <sub>7</sub> H <sub>18</sub> OSi <sub>2</sub>	Me <sub>3</sub> SiCOSiMe <sub>3</sub>	6.41	1556	C <sub>6</sub> H <sub>6</sub> -Me <sub>2</sub> CO-H <sub>2</sub> O	472, 505, 537 <sup>b</sup>
C <sub>10</sub> H <sub>24</sub> GeOSi	Me <sub>3</sub> SiCOGeEt <sub>3</sub>	—	—	MeOH-THF	535 <sup>b</sup>
C <sub>13</sub> H <sub>30</sub> Ge <sub>2</sub> O	Et <sub>3</sub> GeCOGeEt <sub>3</sub>	—	—	C <sub>6</sub> H <sub>6</sub>	464, 495, 527 <sup>b</sup>
C <sub>22</sub> H <sub>24</sub> OSi <sub>2</sub>	Me <sub>3</sub> SiCOSiPh <sub>3</sub>	—	—	C <sub>6</sub> H <sub>12</sub>	480, 517, 550 <sup>b</sup>
C <sub>27</sub> H <sub>26</sub> OSi <sub>2</sub>	Ph <sub>2</sub> MeSiCOSiMePh <sub>2</sub>	—	—	<i>n</i> -C <sub>7</sub> H <sub>16</sub>	524, 554
C <sub>37</sub> H <sub>30</sub> OSi <sub>2</sub>	Ph <sub>3</sub> SiCOSiPh <sub>3</sub>	6.28, 6.42 <sup>c</sup>	1592, 1558	EtOH	517, 545 <sup>b</sup>
				CCl <sub>4</sub>	260-273, 478, 524, 554
		6.43 <sup>d</sup>	1555	C <sub>6</sub> H <sub>6</sub>	518, 548
C <sub>37</sub> H <sub>30</sub> Ge <sub>2</sub> O	Ph <sub>3</sub> GeCOGePh <sub>3</sub>	6.19	1616	C <sub>6</sub> H <sub>12</sub>	248(1590), 254(1952), 260(2290), 265(2180)
				C <sub>6</sub> H <sub>6</sub>	271(1590), 451, 483, 513
					455(18), 485(43), 515(66)

<sup>a</sup> Infrared spectrum was run in CCl<sub>4</sub> unless otherwise noted.

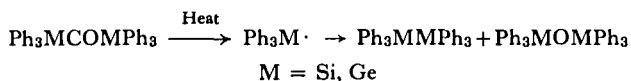
<sup>b</sup> Concentration of solutions unknown so extinction coefficient unknown.

<sup>c</sup> KBr pellet. The shorter wavelength band is of weak intensity, the longer, medium.

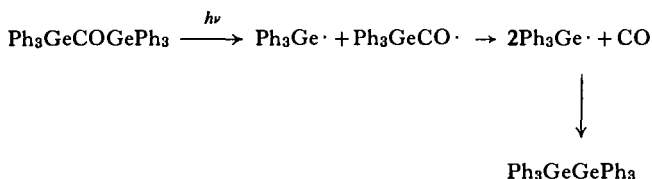
<sup>d</sup> Ethylene dichloride.



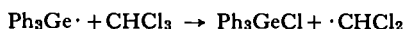
expected carbinol (50) and the germyl ketone was reduced by lithium aluminum hydride to the carbinol in 71% yield (50). At their melting points the bis ketones lose their bright pink or red-orange colors and evolve carbon monoxide. The reaction products from the bis(germyl) ketone were shown to be hexaphenyldigermene and hexaphenyldigermoxane, the former formed by radical coupling and the latter by reaction with incompletely removed oxygen or by radical extraction of oxygen from the ketone by a triphenylgermyl radical, similar to the behavior of silyl radicals observed by Eaborn (88).



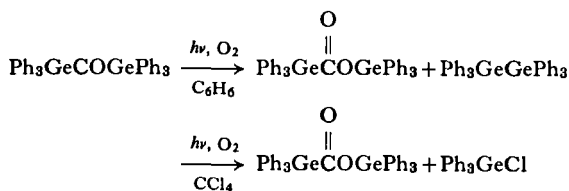
Some preliminary photochemical studies have been made. Photolysis of the bis(germyl) ketone under nitrogen in benzene or methanol led to rapid decolorization of the orange solution and high yields of hexaphenyldigermene, presumably through a Norrish Type I cleavage. When photolyzed



in chloroform under similar conditions, the major product was found to be triphenylchlorogermene, strong evidence for the intermediacy of triphenylgermyl radical, which would be expected by analogy with triphenylsilyl radical (89) or trimethylsilyl radical (88) to abstract halogen from chloroform.



Photolysis of the bis(germyl) ketone in benzene in the presence of air afforded in addition to hexaphenyldigermene, the previously known triphenylgermyl triphenylgermanecarboxylate (90); the latter compound and triphenylchlorogermene were formed in carbon tetrachloride.



The formation of the digermane or chlorogermane suggests the presence of the triphenylgermyl radical, but the mechanism of formation of the ester has not been established. However, in view of the fact that acylgermanes do not readily undergo rearrangements as do their silicon analogs, it seems unlikely that the formation of the ester involves the intermediacy of a germoxycarbene, a type of intermediate used to account for the formation of lactones and esters from acylsilanes (61) (see Section V,E).

## VIII

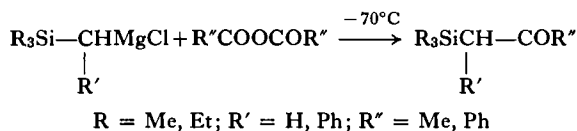
### $\beta$ -KETOSILANES, $\beta$ -KETOGERMANES, AND $\beta$ -KETOSTANNANES

The methods of preparation, and the spectral and chemical properties of  $\beta$ -ketometalloids are summarized in the following sections. Compounds in which a carboxylic acid or ester group are attached through a methylene group to a metalloid atom are not included, although many examples of such compounds are known.

#### A. $\beta$ -Ketometalloid Synthesis

The known examples of  $\beta$ -ketometalloids, summarized in Table XII, have been synthesized by a variety of routes.

Trimethylsilylacetone and related compounds have been prepared by the low-temperature reaction of trialkylsilylmethyl Grignard reagents with acetic anhydride at  $-70^\circ\text{C}$ , although the instability of the compounds has led to some difficulties in isolation at times (43, 63, 91-93).

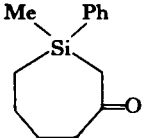


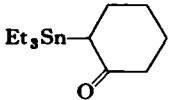
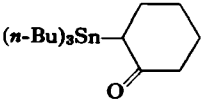
Attempts to obtain a  $\beta$ -ketone from reaction of bis(trimethylsilylmethyl)-cadmium with benzoyl chloride failed (91).

A variety of  $\beta$ -ketosilanes and -germanes have been prepared from the reaction of acylsilanes and acylgermanes with excess diazomethane, as discussed in Section V,D (56).



TABLE XII  
 $\beta$ -KETOSILANES,  $\beta$ -KETOGERMANES, AND  $\beta$ -KETOSTANNANES

Empirical formula	Compound	M.p. or b.p./mm Hg <sup>a</sup> (°C)	Methods of preparation <sup>b</sup>	References
C <sub>6</sub> H <sub>14</sub> OSi	Me <sub>3</sub> SiCH <sub>2</sub> COMe	74°/96	G, H	43, 56, 91, 93
C <sub>7</sub> H <sub>16</sub> OSi	Me <sub>3</sub> SiCH <sub>2</sub> COCH <sub>2</sub> CH <sub>3</sub>	74°–75°/60	H	42
C <sub>9</sub> H <sub>20</sub> OSi	Et <sub>3</sub> SiCH <sub>2</sub> COMe	89°–90°/10	H	93
C <sub>11</sub> H <sub>16</sub> OSi	Me <sub>3</sub> SiCH <sub>2</sub> COPh	104°/3	G, H	56, 63
C <sub>12</sub> H <sub>18</sub> OSi	Me <sub>3</sub> SiCHPhCOMe	101°/5	H	91
C <sub>13</sub> H <sub>18</sub> OSi		110°/0.02	G	29
C <sub>20</sub> H <sub>18</sub> OSi	Ph <sub>3</sub> SiCH <sub>2</sub> CHO	115.5°–116.0°	L	94
C <sub>21</sub> H <sub>20</sub> OSi	Ph <sub>3</sub> SiCH <sub>2</sub> COCH <sub>3</sub>	87°–88.5°	G	56
C <sub>25</sub> H <sub>22</sub> OSi	1-NpPhMeSiCH <sub>2</sub> COPh	54°–56°	G	56
C <sub>26</sub> H <sub>21</sub> ClOSi	Ph <sub>3</sub> SiCH <sub>2</sub> COC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	121°–121.5°	G	56
C <sub>26</sub> H <sub>22</sub> OSi	Ph <sub>3</sub> SiCH <sub>2</sub> COPh	88°–90°	F, G	10, 56
C <sub>27</sub> H <sub>24</sub> O <sub>2</sub> Si	Ph <sub>3</sub> SiCH <sub>2</sub> COC <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	101°–102°	G	56
C <sub>29</sub> H <sub>19</sub> F <sub>9</sub> OSi	( <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> COPh	117°–118.5°	G	56
C <sub>38</sub> H <sub>46</sub> OSi	( <i>p</i> - <i>tert</i> -BuC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> COPh	149°–151°	G	56

C <sub>9</sub> H <sub>20</sub> GeO	Et <sub>3</sub> GeCH <sub>2</sub> COCH <sub>3</sub>	85°–87°/7	I, J	95, 96
C <sub>12</sub> H <sub>26</sub> GeO	<i>n</i> -Pr <sub>3</sub> GeCH <sub>2</sub> COCH <sub>3</sub>	74°–76°/3	I	95
C <sub>14</sub> H <sub>22</sub> GeO	Et <sub>3</sub> GeCH <sub>2</sub> COPh	135°/3	J	96
C <sub>15</sub> H <sub>32</sub> GeO	<i>n</i> -Bu <sub>3</sub> GeCH <sub>2</sub> COCH <sub>3</sub>	106°–107°/1	I	95
C <sub>25</sub> H <sub>22</sub> GeO	1-NpPhMeGeCH <sub>2</sub> COPh	Not distilled	G	29
C <sub>26</sub> H <sub>22</sub> GeO	Ph <sub>3</sub> GeCH <sub>2</sub> COPh	82°–83°	F, G	56
C <sub>9</sub> H <sub>20</sub> OSn	Et <sub>3</sub> SnCH <sub>2</sub> COCH <sub>3</sub>	100.5°–101°/6	K	97
C <sub>12</sub> H <sub>23</sub> OSn	Et <sub>3</sub> Sn- 	116°–117°/4	K	97
C <sub>12</sub> H <sub>26</sub> OSn	( <i>n</i> -Pr) <sub>3</sub> SnCH <sub>2</sub> COCH <sub>3</sub>	98°–100°/1	K	97
C <sub>15</sub> H <sub>32</sub> OSn	( <i>n</i> -Bu) <sub>3</sub> SnCH <sub>2</sub> COCH <sub>3</sub>	130°–132°/2		
		130°–134°/14 <sup>c</sup>	J, K	97
C <sub>17</sub> H <sub>28</sub> OSn	( <i>n</i> -Pr) <sub>3</sub> SnCH <sub>2</sub> COPh	155°–160°/3	J	98
C <sub>18</sub> H <sub>37</sub> OSn	( <i>n</i> -Bu) <sub>3</sub> Sn- 	155°–156°/1	K	97
C <sub>20</sub> H <sub>34</sub> OSn	( <i>n</i> -Bu) <sub>3</sub> SnCH <sub>2</sub> COPh	200°–205°/3	J	98

<sup>a</sup> Reported value is melting point unless value for pressure is given.

<sup>b</sup> Methods of preparation: F, oxidation of  $\beta$ -hydroxymetalloid; G, addition of CH<sub>2</sub>N<sub>2</sub> to acylmetalloid; H, reaction of R<sub>3</sub>SiCHRMgX + acid anhydride; I, R<sub>3</sub>GeI + R<sub>3</sub>SnCH<sub>2</sub>COR; J, R<sub>3</sub>MH + N<sub>2</sub>CH<sub>2</sub>COR; K, R<sub>3</sub>SnOMe + enol acetate; L, isomerization of silyl epoxide with MgBr<sub>2</sub>.

<sup>c</sup> The identity of this compound is uncertain.

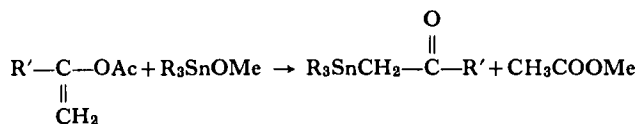
While the reaction with acylgermanes proceeds essentially quantitatively, substantial amounts of the isomeric siloxyalkene are obtained from acylsilanes. Satgé (96) has obtained moderate yields of ketogermanes by reaction of diazoketones with triethylgermane.



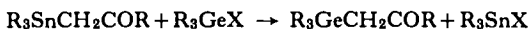
Oxidations of  $\beta$ -hydroxysilanes to the corresponding ketones can be effected but are accompanied by much cleavage of the metalloid-carbon bond. Thus phenacyltriphenylsilane (10) was obtained by chromic acid oxidation and (+)- $\alpha$ -(1-naphthylphenylmethylgermyl)acetophenone, phenacyltriphenylgermane, and phenacyltriphenylsilane were all obtained by oxidation of the corresponding carbinols using *N*-bromosuccinimide in carbon tetrachloride with pyridine or calcium carbonate (29).

Attempted oxidations of  $\beta$ -hydroxysilanes or  $\beta$ -hydroxygermanes using dimethyl sulfoxide with either DCC (dicyclohexylcarbodiimide)—pyridinium trifluoroacetate or acetic anhydride usually fail to give any  $\beta$ -ketometalloid. Acetate esters were detected in the products from the latter reagent (29).

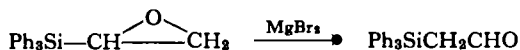
Nesmeyanov (97) has reported the synthesis of a variety of  $\beta$ -ketostannanes by reaction of enol acetates with trialkylmethoxystannanes.



As described in the following section in more detail, reaction of these  $\beta$ -ketostannanes with halogermanes leads to exchange and the formation of  $\beta$ -ketogermanes in good yield (95).



The only  $\beta$ -aldehyde reported, triphenylsilylacetaldehyde, was obtained by rearrangement of a silyl epoxide with a Lewis acid (94).



### B. Spectra of $\beta$ -Ketometalloids

The data for all known compounds are summarized in Table XIII. The infrared carbonyl stretching absorption of  $\beta$ -ketosilanes and -germanes

TABLE XIII  
SPECTRAL PROPERTIES OF  $\beta$ -KETOSILANES, -GERMANES, AND -STANNANES

Empirical formula	Compound	Infrared <sup>a</sup>		Ultraviolet	
		( $\mu$ )	( $\text{cm}^{-1}$ )	Solvent	$\lambda_{\text{max}}(\epsilon)$
C <sub>6</sub> H <sub>14</sub> OSi	Me <sub>3</sub> SiCH <sub>2</sub> COMe	5.92 <sup>c</sup> 5.89 <sup>d</sup>	1690 1698 <sup>d</sup>	C <sub>6</sub> H <sub>12</sub> EtOH	283(81) <sup>b</sup> , 282(57) <sup>c</sup> 276(114) <sup>b</sup>
C <sub>7</sub> H <sub>16</sub> OSi	Me <sub>3</sub> SiCH <sub>2</sub> COCH <sub>2</sub> CH <sub>3</sub>	—	—	C <sub>6</sub> H <sub>12</sub> EtOH	279(93) 276(121)
C <sub>9</sub> H <sub>20</sub> OSi	Et <sub>3</sub> SiCH <sub>2</sub> COMe	5.92	1690	<i>e</i>	282(72) <sup>c</sup>
C <sub>11</sub> H <sub>16</sub> OSi	Me <sub>3</sub> SiCH <sub>2</sub> COPh	6.00	1666	C <sub>6</sub> H <sub>12</sub>	321.5(116), 333.5(108), 347.5(66), 363.5(20)
C <sub>20</sub> H <sub>18</sub> OSi	Ph <sub>3</sub> SiCH <sub>2</sub> CHO	5.88	1700	—	—
C <sub>21</sub> H <sub>20</sub> OSi	Ph <sub>3</sub> SiCH <sub>2</sub> COCH <sub>3</sub>	5.90	1695	C <sub>6</sub> H <sub>12</sub>	293(s)(182), 302(s)(138)
C <sub>25</sub> H <sub>22</sub> OSi	1-NpPhMeSiCH <sub>2</sub> COPh	6.00	1667	C <sub>6</sub> H <sub>12</sub>	314(169), 318(89)
C <sub>26</sub> H <sub>21</sub> ClOSi	Ph <sub>3</sub> SiCH <sub>2</sub> COC <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>	6.00	1667	C <sub>6</sub> H <sub>12</sub>	316(s)(293)
C <sub>26</sub> H <sub>22</sub> OSi	Ph <sub>3</sub> SiCH <sub>2</sub> COPh	6.00	1667	EtOH	310(s)(328)
C <sub>27</sub> H <sub>24</sub> O <sub>2</sub> Si	Ph <sub>3</sub> SiCH <sub>2</sub> COC <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	5.98	1674	C <sub>6</sub> H <sub>12</sub>	314(312), 322(280)
C <sub>29</sub> H <sub>19</sub> F <sub>9</sub> C <sub>2</sub> Si	( <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> COPh	5.98	1674	C <sub>6</sub> H <sub>12</sub>	318(157), 330(143)
C <sub>38</sub> H <sub>46</sub> OSi	( <i>p</i> - <i>tert</i> -BuC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> COPh	6.00	1667	—	—
C <sub>9</sub> H <sub>20</sub> GeO	Et <sub>3</sub> GeCH <sub>2</sub> COCH <sub>3</sub>	5.90	1695	<i>e</i>	283(123)
C <sub>12</sub> H <sub>26</sub> GeO	<i>n</i> -Pr <sub>3</sub> GeCH <sub>2</sub> COCH <sub>3</sub>	5.93	1686	<i>e</i>	280(115)
C <sub>15</sub> H <sub>32</sub> GeO	<i>n</i> -Bu <sub>3</sub> GeCH <sub>2</sub> COCH <sub>3</sub>	5.91	1692	<i>e</i>	280(117)
C <sub>25</sub> H <sub>22</sub> GeO	1-NpPhMeGeCH <sub>2</sub> COPh	6.02	1661	C <sub>6</sub> H <sub>12</sub>	314(490), 318(230)
C <sub>26</sub> H <sub>22</sub> GeO	Ph <sub>3</sub> GeCH <sub>2</sub> COPh	6.02	1660	C <sub>6</sub> H <sub>12</sub>	320.5(229), 332(s)(209), 345(s)(132), 362(s)(46)
C <sub>9</sub> H <sub>20</sub> OSn	Et <sub>3</sub> SnCH <sub>2</sub> COCH <sub>3</sub>	5.94	1684	<i>e</i>	280(219)
C <sub>15</sub> H <sub>32</sub> OSn	<i>n</i> -Bu <sub>3</sub> SnCH <sub>2</sub> COCH <sub>3</sub>	5.94	1686	<i>e</i>	283(120)

<sup>a</sup> Infrared spectra were taken in CCl<sub>4</sub>.

<sup>b</sup> Data from Musker and Ashby (42).

<sup>c</sup> Data from Litvinova *et al.* (93).

<sup>d</sup> Data from Musker and Larson (43).

<sup>e</sup> Solvent not known.

occurs at longer wavelength than with their carbon analogs, but is at considerably shorter wavelength than that of acylmetalloids. Some typical data are given in Table XIV.

TABLE XIV  
INFRARED WAVELENGTHS OF CARBONYL STRETCHING  
ABSORPTION

Class	M = C	Si	Ge
Ph <sub>3</sub> MCH <sub>2</sub> COPh	5.89 $\mu^a$	6.00 $\mu^a$	6.02 $\mu^b$
Me <sub>3</sub> MCH <sub>2</sub> COMe <sup>c</sup>	5.82 $\mu$	5.89 $\mu$	—

<sup>a</sup> Brook and Pierce (10).

<sup>b</sup> Brook and MacRae (29).

<sup>c</sup> Musker and Larson (43).

The cause of this phenomenon can undoubtedly be attributed, at least in part, to inductive effects due to the low electronegativity of the silyl group (10), but it has been suggested, based also on ultraviolet (42) and NMR data, that "intramolecular interaction between the nonbonding electrons of the ketone oxygen and the *d* orbitals of silicon occur in the compounds" (43), i.e.,  $\sigma(p-d)$  bonding.

While not as yet extensively studied, the ultraviolet spectra of  $\beta$ -keto-metalloids appear to be very similar to those of their carbon analogs, the position of both  $n-\pi^*$  and  $\pi-\pi^*$  absorptions falling within a few millimicrons of the positions for the carbon compound. However, Musker (42) has noted that the extinction coefficients of the  $n-\pi^*$  transitions in  $\beta$ -ketosilanes are considerably greater (by a factor of 4-5) than for the carbon analogs, and this phenomenon is attributed to "perturbation of the carbonyl group by the silicon *d* orbitals which results in a mixing of the *s* and *np* orbital character of the carbonyl oxygen making the electronic transition more allowed." The relatively facile thermal rearrangements of  $\beta$ -keto-silanes to the isomeric siloxyalkenes (57) (see Section V,D) might also be considered as additional evidence for a ground state silicon-oxygen interaction. However, these speculations must be made with some caution.  $\beta$ -Ketogermanes and -silanes have very similar infrared and ultraviolet spectra, suggesting on the basis of the above argument, that similar metalloid-oxygen interactions should exist in both types of compound. Thus it would be predicted that ketogermanes would similarly rearrange. However

vigorous heating of  $\beta$ -ketogermanes fails to lead to any thermal rearrangement to a germyoxyalkene and thus no parallel between spectral properties and chemical behavior exists. Hence it is not clear what inferences about intramolecular interaction can be drawn from either chemical behavior or spectral properties.

In their NMR spectra alkyl protons of  $\beta$ -ketometalloid compounds show some effects due to a neighboring metalloid atom. Methylene protons between the metalloid atom and the carbonyl group ( $M-CH_2CO$ ) are less deshielded than in the carbon compounds, as might be expected from the presence of the neighboring metalloid atom: alkyl groups attached to the carbonyl group on the side remote from the metalloid atom ( $MCH_2COMe$ ) do not appear to feel the presence of the metalloid atom. Some typical data are given in Table XV.

TABLE XV  
NUCLEAR MAGNETIC RESONANCE POSITIONS<sup>a</sup>

Class	M = C	Si	Ge
$Me_3MCH_2COCH_3^b$	1.92	1.92	—
$Me_3MCH_2COMe^b$	2.20	2.08	—
$Ph_3MCH_2COCH_3$	—	1.68	—
$Ph_3MCH_2COMe$	—	2.88	—
$Me_3MCH_2COPh$	—	2.62	—
$Ph_3MCH_2COPh$	4.42 <sup>c</sup>	3.49 <sup>c</sup>	3.48 <sup>c</sup>
$R_3M^*CH_2COPh^d$	—	3.25	3.40

<sup>a</sup> Positions given as  $\delta$ , in ppm below TMS, used as an internal standard in carbon tetrachloride unless otherwise noted.

<sup>b</sup> Musker and Larson (43).

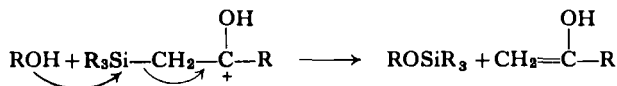
<sup>c</sup>  $CDCl_3$  solvent.

<sup>d</sup>  $R_3M^* = 1-NpPhMeSi$  or  $Ge$ .

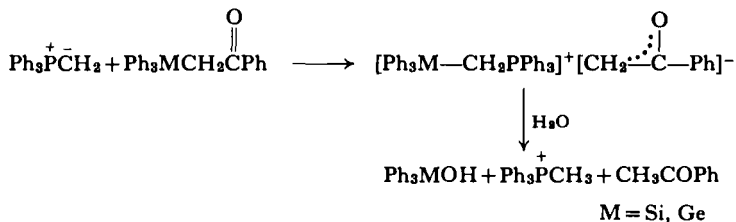
### C. Chemical Properties of $\beta$ -Ketometalloids

Studies of the chemical behavior of  $\beta$ -ketometalloid compounds have not been extensive to date. The compounds are relatively unstable to both acid and base, the acyl group being cleaved from the metalloid (91, 99, 100). Similar behavior was reported for the reaction of the ketones phenacyltriphenylsilane and phenacyltriphenylgermane with methylenetriphenylphosphorane, since the major product of the reactions was the ketone



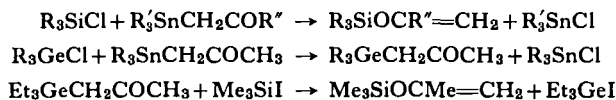


acetophenone; none of the normal Wittig product, an alkene, was obtained. The mechanism proposed involved nucleophilic attack on the metalloid atom (11) by the electron-rich carbon of the alkylidenephosphorane, resulting in displacement of an enolate anion.



The lithium aluminum hydride reduction of a  $\beta$ -ketogermane has been reported (95) but similar reductions of  $\beta$ -ketostannanes are reported to result in cleavage (98).

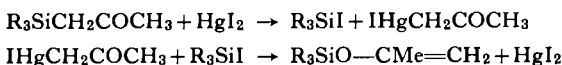
Some exceedingly interesting rearrangements of  $\beta$ -ketometalloids (or the related esters) have been described in the last few years by Baukov and Lutsenko. The reaction of metalloid halides with metalloid carbonyl compounds may yield, depending on the metalloid halide, either the  $\beta$ -ketone or the related oxyalkene. The following examples are typical:



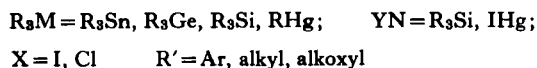
Chlorosilanes are reported to react with  $\beta$ -ketostannanes to give in most cases the siloxyalkenes (95, 101), whereas chlorogermanes yield only the  $\beta$ -ketogermane (95). On the other hand,  $\beta$ -ketogermanes react with silyl iodides (chlorides are less reactive) to give rearranged siloxyalkenes (95).

Recently Baukov has also reported that  $\beta$ -ketosilanes are rearranged, using mercuric iodide as catalyst, to the isomeric siloxyalkene (93, 102). The reaction was suggested to occur in two stages, the first yielding trialkylsilyl

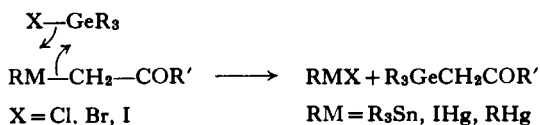
iodide, which subsequently reacted further; consistent with this mechanism, the rearrangement was found to be catalyzed also by trialkylsilyl iodides.



While little has been written by the Russian group regarding the mechanisms of the reactions, most of the data are readily accommodated by processes involving six-membered transition states. Thus nucleophilic attack on the metal or metalloid atom N by the carbonyl oxygen with displacement of halide from one metalloid to the other would account for the formation of the oxyalkene isolated.

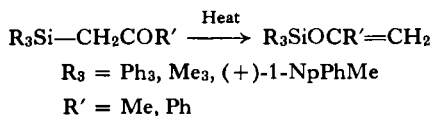


While this accounts satisfactorily for the behavior of silicon compounds, and suggests again, as in the acylmetalloids, that silicon-oxygen bond formation is a powerful driving force governing the reactions of these compounds, the behavior of  $\beta$ -ketones with germanium halides is not explained, and appears to require a four-center transition state.

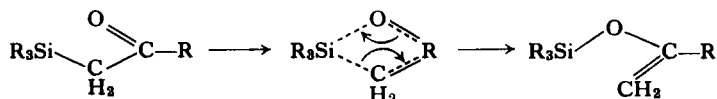


Thus there appears to be no tendency to form germanium-oxygen bonds in reactions of either acylgermanes or  $\beta$ -ketogermanes.

Recently we have observed that  $\beta$ -ketosilanes, but not  $\beta$ -ketogermanes, can be isomerized thermally to the analogous oxyalkenes (57). This kind of rearrangement had previously been proposed by Brook and Pierce to



account for thermal isomerization of products derived photochemically from diphenylsilacyclohexanone-2 (61) (see Section V,E). The rearrangement has been shown to involve retention of configuration at an asymmetric silicon center, and to proceed by clean first-order kinetics. Thus this rearrangement must be intramolecular and must involve a four-center



transition state. The temperatures required for these isomerizations ( $80^\circ\text{--}140^\circ\text{C}$ ) were considerably greater than those used by Baukov in his catalyzed reactions, indicating true participation of the mercuric iodide or trialkylsilyl iodide in the latter reactions. Baukov has recently reported similar observations (102).

## IX

### SUMMARY

From the preceding material it is evident that there is much of interest both chemically and spectroscopically in the behavior of acylmetalloids and  $\beta$ -ketometalloids. Silicon compounds show unusual chemical behavior, quite different from their germanium analogs, which generally behave rather like carbon ketones. Not enough is known of the tin compounds to have any idea whether their chemistry will be like that of silicon or germanium, although the latter possibility seems more likely. Spectroscopically, all metalloid ketones are very similar to each other and, particularly with the acylmetalloids, outstandingly different from the carbon analogs. This behavior appears to be best interpreted as due to inductive effects arising from the relatively low electronegativities of the metalloid atoms compared to carbon. While contributions from  $\pi(\pi-d)$  bonding between the carbonyl group and the metalloid atom may play some role in determining the properties of the acylmetalloids, this effect does not seem to be the major one, and several different attempts to detect  $\pi$ -bonding either failed or were inconclusive. It is also possible that  $\sigma(p-d)$  bonding between the unshared electrons in oxygen and the  $d$  orbitals on the metalloid atom play some role in governing the behavior of both acylmetalloids and  $\beta$ -ketometalloids, in particular the intensities of their spectroscopic transitions, but the importance of this effect cannot be evaluated. Future studies must

inevitably reveal further interesting behavior and a better understanding of the observed phenomena.

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# ***$\sigma$ -Alkyl and -Aryl Derivatives of Transition Metals***

G. W. PARSHALL and J. J. MROWCA

*Central Research Department  
E. I. du Pont de Nemours and Company  
Wilmington, Delaware*

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## **I**

### **INTRODUCTION**

Research on alkyl and aryl derivatives of the transition metals has flourished in recent years. The last fully comprehensive review of this area was prepared by Coates (1) in 1960, although excellent reviews of individual areas have appeared recently. For example, King (2) discussed metathetical syntheses of alkyl complexes, Heck (3) has described alkyl and acyl cobalt compounds, and Cross (4) has summarized the chemistry of platinum derivatives. Tabulations of individual organometallic compounds have been assembled by Dub (5) and Kritskaya (6).

The purpose of this chapter is to bring perspective to this field by summary of the chemistry of the metal-carbon *sigma* bond with emphasis on the reactions common to most alkyl and aryl derivatives of transition metals. Individual variations occur, but synthetic methods such as meta-thesis of a metal chloride with a Grignard reagent or aryllithium are common to many types of transition metal complexes. Similarly, most M—C bonds react with water, hydrogen halides, and halogens, although substantial rate differences occur. The discussion will include alkyl, aryl, and acyl derivatives but in general excludes perfluoroalkyl and  $\pi$ -allyl compounds. Fluoroalkyl derivatives have been reviewed by Treichel and Stone (7), pentafluorophenyl compounds by Chambers and Chivers (8), and allyl metal complexes by Green and Nagy (9) and Fischer and Werner (10).

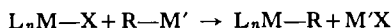
## II

### GENERAL PREPARATIVE METHODS

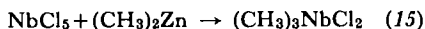
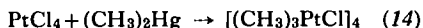
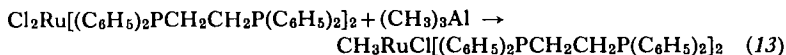
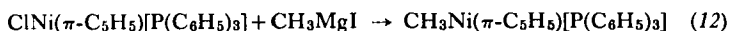
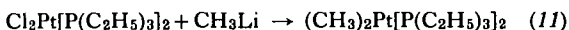
A wide variety of methods have been used to synthesize complexes containing transition metal-carbon  $\sigma$ -bonds. This section will deal only with the formation of the metal-carbon bond, i.e., transformations of compounds with existing metal-carbon bonds to give new complexes will not be discussed.

#### A. Reactions of Anionic Alkylating Agents with $L_nM-X$

By far the most widely applied method for the formation of metal-carbon  $\sigma$ -bonds is the reaction of a metal-X compound where X is a halide or some other leaving group, with an anionic alkylating agent.

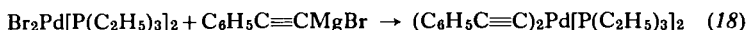
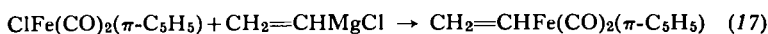
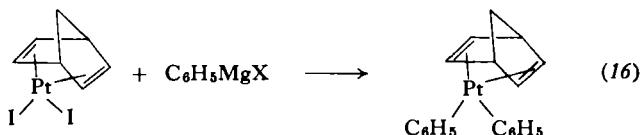


Alkylating agents that have been used include organo compounds of alkali metals, magnesium, aluminum, mercury, and zinc. The following equations illustrate some examples:

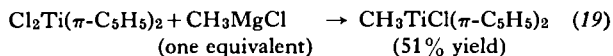




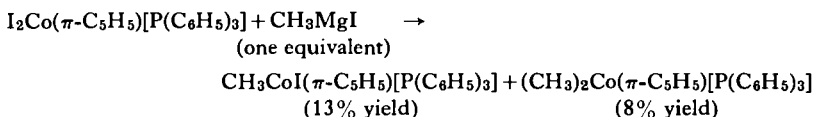
R groups other than simple alkyls may be introduced by using aryl, alkenyl, or alkynyl reagents.



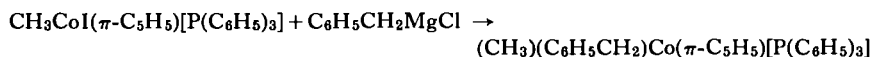
When there is more than one leaving group and consequently a chance to form more than one metal-carbon bond, it is sometimes possible to control the amount of alkylation by limiting the quantity of alkylating agent.



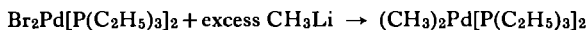
However, treatment of  $\pi$ -cyclopentadienyldiiodotriphenylphosphinecobalt-(III) with one equivalent of methylmagnesium iodide gives almost equal yields of mono- and dimethylated products (20).



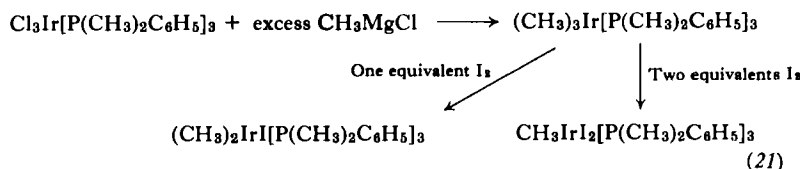
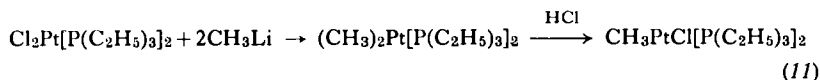
Interestingly, reaction of  $\text{CH}_3\text{CoI}(\pi\text{-C}_5\text{H}_5)[\text{P}(\text{C}_6\text{H}_5)_3]$  with benzylmagnesium chloride affords a rare example of a mixed dialkyl complex (20).



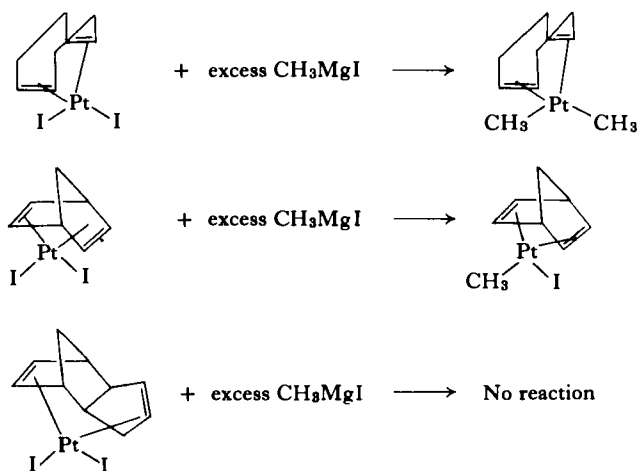
The degree of alkylation often depends on the activity of the alkylating reagent. For example, in the synthesis of methylpalladium compounds, methyl lithium is more reactive than the corresponding Grignard reagent (18).



An alternative method of selective alkylation is to peralkylate the transition metal halide complex and then to cleave alkyl groups from the product under carefully controlled conditions.



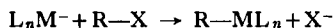
Surprisingly subtle changes in the structure of the starting transition metal halide complex can affect the course of the alkylation reaction (16).



These last examples illustrate the status of the art in the synthesis of metal-carbon bonds by the anionic alkylating agent method—it is often difficult to predict the outcome of the reaction. Mechanistic study of this method seems warranted.

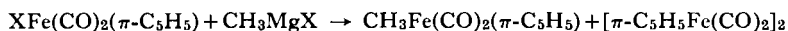
### B. Reactions of Transition Metal Complex Anions with $\text{RX}$

Metal complex anions often react with  $\text{RX}$  species in which  $\text{X}$  is a halide or other leaving group to form metal-carbon  $\sigma$ -bonds.

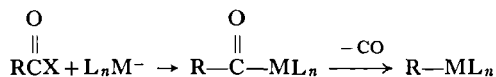


This reaction is formally inverse to that of Section II, A, and several compounds have been prepared by both methods. When faced with a choice,

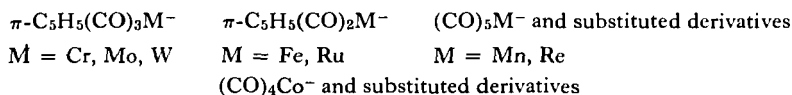
however, the metal anion + RX method is preferred since it usually gives the metal alkyl in higher yield. Lower yields in the  $M-X + R^-$  method result from competitive reduction of the metal complex to dimeric by-product (22).



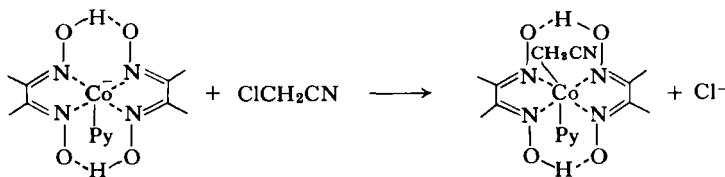
By varying the metal complex anion and RX, a wide variety of metal compounds containing transition metal-carbon  $\sigma$ -bonds have been prepared directly by this reaction. In addition, acyl metal derivatives prepared by this method may be decarbonylated to give alkyl and aryl metal complexes.



The metal carbonyl anions and their substituted derivatives, an area recently reviewed by King (2), dominate this synthetic route. The most commonly used anions are



Examples of the use of noncarbonyl anions can be found in the work of Schrauzer and Windgassen on cobalt complexes bearing the dimethylglyoximate ligand (23, 24)



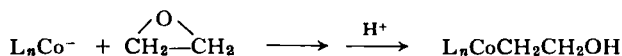
and in the work of Calderazzo and Floriani on  $N,N'$ -ethylenebis(salicylideneiminato)cobalt complexes (25).

A semiquantitative estimation of the relative nucleophilicities of a series of transition metal anions has been made by measuring the rates of their reactions with alkyl halides (26). The observed nucleophilicities decreased in the order  $\pi-C_5H_5(CO)_2Fe^- > \pi-C_5H_5(CO)_2Ru^- > \pi-C_5H_5(CO)Ni^- > (CO)_5Re^- > \pi-C_5H_5(CO)_3W^- > (CO)_5Mn^- > \pi-C_5H_5(CO)_3Mo^- > \pi-C_5H_5(CO)_3Cr^- > (CO)_4Co^- > (CO)_5(CN)Cr^-, (CO)_5(CN)Mo^-,$

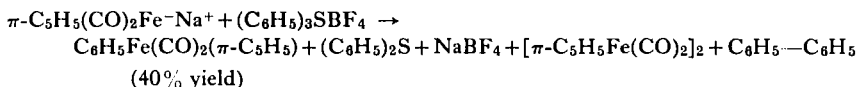
$(\text{CO})_5(\text{CN})\text{W}^-$ . Results of this kind should be of predictive value in synthesis.

Variations in the  $\text{R}-\text{X}$  reactant include alkyl, aryl, alkenyl, benzyl, allyl, and propargyl halides. The reactivity of the halogen atom, of course, influences these reactions greatly; phenyl or vinyl halides are sluggish compared to the more reactive alkyl, benzyl, allyl, and propargyl halides. For example, reaction of  $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}^-$  with methyl iodide gives a 70% yield of the methyliron complex, but reaction with iodobenzene only yields 2% of the phenyliron complex (22).

Other substrates which react with metal complex anions to give metal-carbon bonds are sulfates, epoxides, and onium compounds. Ethylene oxide gives  $\beta$ -hydroxyethyl compounds (27, 28).



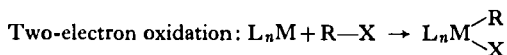
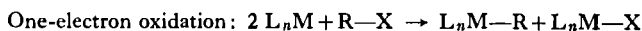
Reactions with onium compounds have not been widely investigated (29); however, in a study on the arylation of  $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{FeNa}$ , it was found that the yield of phenyliron complex increased in the order  $\text{C}_6\text{H}_5\text{N}_2\text{BF}_4 < (\text{C}_6\text{H}_5)_2\text{IBF}_4 < (\text{C}_6\text{H}_5)_3\text{SBF}_4$  while the yield of by-product  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  decreased (30). The overall reaction for the triphenylsulfonium compound is



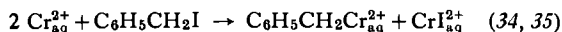
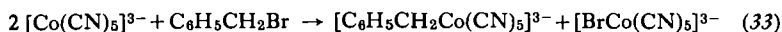
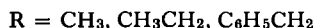
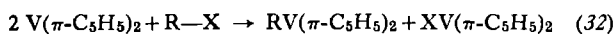
The yield compares favorably with other methods used to prepare this compound (22, 31).

### C. Oxidative Reactions

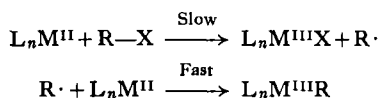
One of the most interesting methods of forming the transition metal-carbon  $\sigma$ -bond is the oxidation of a metal complex from a low to a higher valent state with concomitant metal-carbon bond formation. Both one- and two-electron oxidations have been observed, the latter being the well known "oxidative addition" reaction.



One-electron oxidation reactions to form metal-carbon bonds have been reported for vanadium, cobalt, and chromium. Some examples are

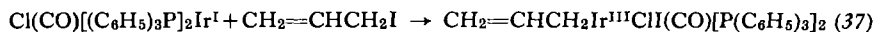
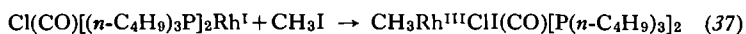


Mechanistic studies on the cobalt (36) and chromium (35) oxidations reveal a free radical mechanism for these reactions.

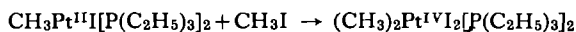
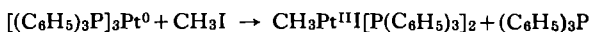


As in other oxidation reactions, reaction rates increase with decreasing carbon-halogen bond strength. The relative rates of reactions of the halides decrease in the order tertiary > secondary > primary and  $\text{I} > \text{Br} > \text{Cl}$ .

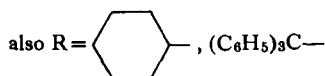
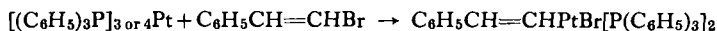
Oxidative addition reactions to form metal alkyls or aryls have been observed for low-valent rhodium (37, 38), iridium (37, 39, 40), ruthenium (41), nickel (42), and platinum (11, 43, 44) complexes. Reactions with perfluoroalkyl halides extend this list to cobalt (45) and iron (46). Some examples are



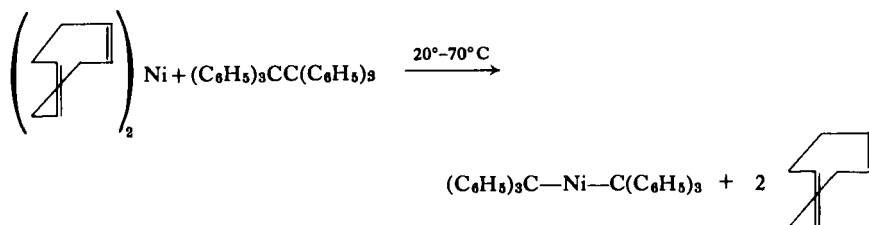
In addition, Chatt and Shaw have reported a series of reactions in which platinum undergoes complete oxidation from Pt(0) to Pt(IV) by two two-step oxidation reactions (11).



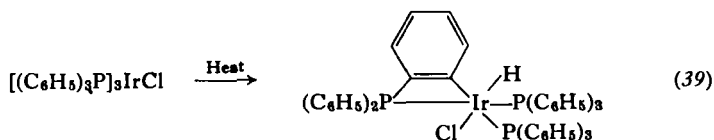
In an interesting extension of the oxidative addition reaction, Cook and Jauhal prepared several platinum-carbon compounds which were not available by conventional reactions. They prepared styryl, trityl, and cyclohexyl compounds of platinum(II) which could not be obtained by the anionic alkylating route (44).



The oxidative addition reaction to form metal-carbon  $\sigma$ -bonds is not restricted to the addition of alkyl halides. Wilke and Schott have found an unusual oxidative addition of a symmetrical oxidant, hexaphenylethane, to zero-valent nickel to give a nickel(II) dialkyl of remarkable stability (42).



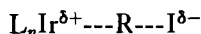
Compounds with active hydrogens may also undergo the reaction.



Chock and Halpern (47) initiated a mechanistic study of the oxidative addition reaction by examining the kinetics of the reaction of *trans*- $\text{X}(\text{CO})[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ir}$  where X is Cl, Br, and I with alkyl halides. In the reaction with  $\text{CH}_3\text{I}$



it was found that the rate decreased in the order  $\text{Cl} > \text{Br} > \text{I}$  and increased on going from solvent benzene to dimethylformamide. The rate with  $\text{CH}_3\text{Br}$  was too slow for measurement. The solvent dependence and activation parameters suggest a highly polar transition state



rather than the alternative

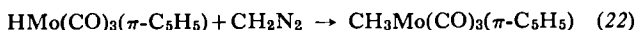
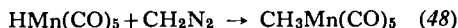


for these reactions. The stereochemistry of these reactions is unknown.

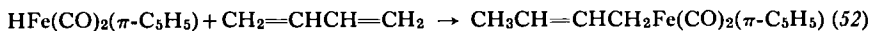
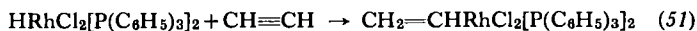
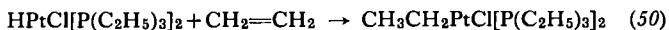
### D. Insertion Reactions

Transition metal-carbon  $\sigma$ -bond formation by this method most commonly involves the insertion of some carbon-containing species into a metal-hydrogen bond. The name "insertion reaction" for this process has no mechanistic significance but merely describes the outcome of the reaction. This method of bond formation, while not the most widely applied for the synthesis of metal alkyls, is nevertheless significant because it is often a key step in transition metal-catalyzed reactions of olefins such as Ziegler-Natta polymerization, hydrogenation, carbonylation, dimerization, and isomerization.

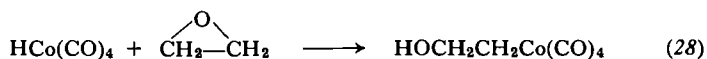
Examples of inserting species are carbenes, olefins, acetylenes, and epoxides. Reaction of diazomethane with metal hydrides or halides has given several alkylmetal complexes, for example,



However, because of the difficulties involved in handling this reagent, other methods for preparing these compounds are generally preferred. Olefins and acetylenes insert into metal-hydrogen bonds to give alkyl and alkenyl complexes, respectively. Examples are



Epoxides give  $\beta$ -hydroxyalkyl compounds.



The success of these reactions depends on their nonreversibility under the isolation conditions. In some cases, alkyl formation can only be inferred from spectroscopic measurements (53).

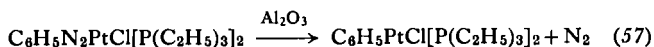
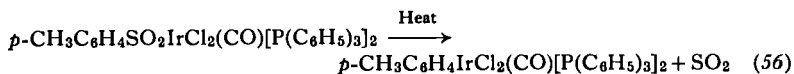
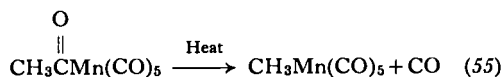
Little success has been achieved in the synthesis of alkyl metal complexes by insertion reactions into metal-carbon bonds. This is due undoubtedly to further reactions of the immediate insertion products to give polyinsertion or decomposition products. The insertion of olefins and acetylenes into metal-carbon bonds to give new alkyl or vinyl derivatives is discussed in Section IV,B.

Finally, insertion of acetylenes into titanium- and zirconium-nitrogen bonds affords isolable alkenyl complexes (54).

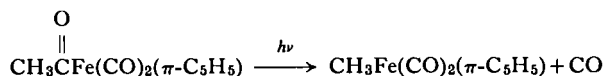
### E. Elimination Reactions

Expulsion of a moiety separating metal and carbon atoms with resulting metal-carbon bond formation is another method for preparing  $\sigma$ -bonded metal complexes. Here again, the name "elimination reaction" for this process has no mechanistic significance.

Reactions eliminating CO, SO<sub>2</sub>, N<sub>2</sub>, and, in one case, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn have been reported. Some illustrations of these are as follows:



The thermal elimination reactions often occur under relatively mild conditions (<150° C). For resistant compounds, photolysis is sometimes employed (31).

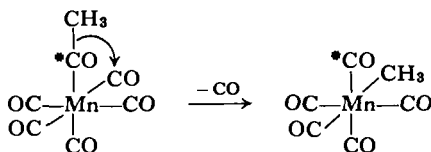


Interestingly, despite the fact that RCOMn(CO)<sub>5</sub> compounds decarbonylate easily, an attempt to eliminate CO<sub>2</sub> from C<sub>2</sub>H<sub>5</sub>OOCMn(CO)<sub>5</sub> was unsuccessful (59). Carbon dioxide elimination from carboxylate complexes to give alkyl or aryl derivatives has not been reported.

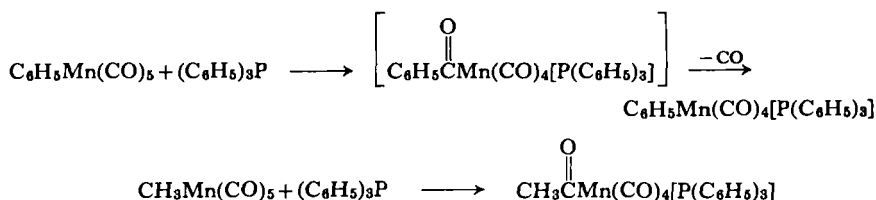
Synthetic and mechanistic studies have concentrated on the decarbonylation reaction of acylmanganese and -rhenium complexes. In addition, mechanistic results on the carbonylation reaction (Section IV,B,1), through the principle of microscopic reversibility, have been applied to the decarbonylation reaction. From these investigations two important points have emerged concerning the mechanism of the decarbonylation reaction of acylmanganese carbonyl complexes: (1) the outgoing CO molecule is not the carbonyl group of the metal-acyl system but is one of the coordinated carbon monoxide molecules, (2) the decarbonylation occurs by an alkyl



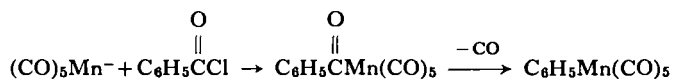
group migration in which the acyl CO retains its original coordination site on the manganese (60).



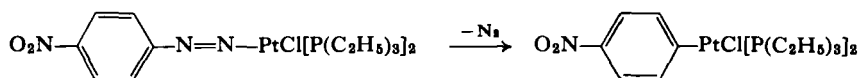
Aryl compounds appear to undergo elimination reactions more readily than alkyl compounds. This difference in reactivity is probably due to the greater migratory aptitude of the aryl group. For example, treatment of  $\text{C}_6\text{H}_5\text{Mn}(\text{CO})_5$  with triphenylphosphine gives the substituted phenylmanganese complex as the isolated product (61). In contrast, the analogous methyl complex gives the acetylmanganese compound (61, 62).



The synthetic utility of the elimination reaction is enhanced by its usefulness in preparing a number of compounds difficult or impossible to synthesize by other methods. For example, in the preparation of  $\text{RMn}(\text{CO})_5$  compounds by the reaction of  $\text{XMn}(\text{CO})_5$  with anionic alkylating agents, reduction of  $\text{XMn}(\text{CO})_5$  to  $\text{Mn}_2(\text{CO})_{10}$  lowers the yields (63). The alternative route of reacting the metal carbonyl anion with an acid chloride and then decarbonylating the resulting acyl complex is often more desirable (55, 64).



In another example, the loss of  $\text{N}_2$  from arylazo platinum complexes provides a method for the formation of arylplatinum compounds not accessible by the usual Grignard route (57).



## III

## PHYSICAL PROPERTIES

Although a wide range of physical techniques have been applied to the characterization of organometallic compounds, nuclear magnetic resonance and infrared spectroscopy are by far the most successful for characterization of the organic ligand. Most other techniques such as dipole moment and electronic spectroscopy describe the complex as a whole. Electron spin resonance and magnetic moment studies are limited to the fairly narrow range of paramagnetic organometallics. Only mass spectrometry seems to have much untapped utility for the characterization of alkyl and aryl ligands in transition metal complexes.

One special characteristic of the alkyl or aryl ligand is that it is a strong  $\sigma$ -donor in the context of crystal-field theory. As a consequence, it lies high in the "spectroscopic series" in electronic spectroscopy and it has a strong "trans effect" in terms of weakening a metal-ligand bond trans to itself in a square-planar or octahedral complex. The trans effect is observable in the low force constants found for M—X bonds trans to alkyl or aryl groups. Even more directly, crystal structure studies have shown that M—X bonds trans to organic ligands are longer than cis M—X bonds. Trans interactions also affect chemical shift phenomena in NMR spectra and the rates of solvolyses of anionic ligands in organometallic compounds.

In addition to brief discussions of physical techniques as applied to organic derivatives of the transition metals, we include a short section on stability of these compounds.

### A. Spectral Properties

#### 1. Nuclear Magnetic Resonance

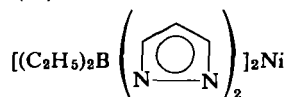
The proton magnetic resonance spectrum is a powerful tool for determination of the nature of a hydrocarbon group in organometallic compounds (65). Its application for this purpose is very similar to its use in organic chemistry. The use of  $^{19}\text{F}$  spectra has been described in the review of fluoroalkyl metal compounds by Treichel and Stone (7). Other nuclei such as  $^{31}\text{P}$ ,  $^{55}\text{Mn}$ , and  $^{59}\text{Co}$  have given useful information on molecular configuration and electron distribution in organometallic compounds but they provide little help in the characterization of the C—M bond.

The chemical shifts of protons on carbons bound to transition metals vary widely. The values<sup>1</sup> reported for  $\text{CH}_3\text{—M}$  protons range from  $\tau 7.12$  in  $\text{CH}_3\text{RhCl}(\text{PPh}_3)_2(\text{CH}_3\text{I})$  (38) to  $\tau 12.1$  in  $\text{CH}_3\text{Ni}(\pi\text{-C}_3\text{H}_5)$  (68). In higher alkyl derivatives, it is common to find a high-field shift of the  $\alpha$ -protons even though the signals of more remote protons are found in the ranges observed for analogous groups in organic compounds. As a result, the  $\text{CH}_2$  absorption of an ethyl group may coincide with the  $\text{CH}_3$  signal, as in  $\text{C}_2\text{H}_5\text{Mn}(\text{CO})_5$  ( $\tau 8.69$ ) (69), or actually lie at higher field, as observed for  $(\text{C}_2\text{H}_5)_2\text{Ni}(\text{bipy})$  ( $\tau_{\text{CH}_2} 9.20$ ,  $\tau_{\text{CH}_3} 8.95$ ) (70). This high-field shift has been correlated with the electronegativity of the metal. On the basis of the chemical shifts for the nickel complex, Saito *et al.* (70) assign an electronegativity of 1.9 to the nickel-bipyridine moiety, a value close to that (1.8) which Pauling assigns to nickel itself (71).

The chemical shift of a methyl group bound to a transition metal is strongly dependent on the nature of the other ligands on the metal atom. In the series  $\text{CH}_3\text{TiX}(\text{C}_5\text{H}_5)_2$ , the methyl absorption shifts to high field as the halide is varied from Cl to Br to I (19). The opposite trend is observed in the tetrameric methylplatinum compounds  $[(\text{CH}_3)_3\text{PtX}]_4$  (72). In the dimethylglyoximate (DMG) complexes  $\text{CH}_3\text{CoL}(\text{DMG})_2$ , the chemical shift of the  $\text{CH}_3$  signal varies with nature of the neutral trans ligand,  $\text{H}_2\text{O} > \text{pyridine} > \text{P}(\text{OCH}_3)_3 > \text{P}(n\text{-C}_4\text{H}_9)_3 > \text{P}(\text{C}_6\text{H}_5)_3$  (23).

Metal-hydrogen coupling constants have been useful in determining whether or not an alkyl group is bonded directly to a metal atom. For example, the two methyl absorptions of  $\text{CH}_3\text{RhCl}(\text{PPh}_3)_2(\text{CH}_3\text{I})$  were distinguished by the fact that the low-field signal was a triplet ( $J_{\text{P-H}} = 5.1$  cps) further split into doublets ( $J_{\text{Rh-H}} = 2.4$  cps) (38). This criterion also establishes the presence of metal-carbon bonds in some rhodium and platinum acetylacetonates (73, 74). This application is largely confined to compounds of rhodium, platinum, and tungsten which have significant abundances of isotopes with nuclear spins of 1/2. In general, platinum-hydrogen coupling constants are much larger (70–90 cps) than those observed with rhodium compounds.

<sup>1</sup> Even lower values have been reported for the  $\alpha\text{-CH}_2$  protons in  $(\text{CO})_5\text{MnCH}_2\text{CH}_2\text{CH}_2\text{—Mn}(\text{CO})_5$  (66). However, these exceptionally low values probably result from paramagnetic shifts caused by metal atom field effects on protons close to but not bonded to the metal. A similar effect has been noted (67) for  $\text{CH}_2$ 's of



In addition to providing structural evidence about the nature of an alkyl group bound to a metal, the NMR spectrum also reflects electronic interactions between various ligands. The chemical shifts of methyl protons described above probably arise through polarization of the C—M  $\sigma$ -bond. With aryl metal compounds, the situation is more complex because  $\pi$ -bonding can also occur between arene  $\pi$ -orbitals and metal  $d$  orbitals. This effect is noted in a study (19) of the chemical shift of the  $\text{C}_5\text{H}_5$  signal in a series of *m*- and *p*-substituted aryl compounds  $(\text{XC}_6\text{H}_4)_2\text{Ti}(\pi\text{-C}_5\text{H}_5)_2$ . Although some correlation was noted between  $\delta_{\text{C}_5\text{H}_5}$  and the Hammett  $\sigma$ -parameter of X, a better fit was obtained with a combination of Taft inductive and resonance parameters. The effect is more dramatic in *trans*- $\text{FC}_6\text{H}_4\text{PtX}(\text{PEt}_3)_2$  compounds. The  $^{19}\text{F}$  shielding parameters of the *m*- and *p*-fluorophenyl derivatives permit a more direct evaluation of the electronic interaction between an anionic ligand and the metal (75). In both the titanium and platinum compounds, the metal atom appears to release electron density to the aromatic ring.

## 2. Infrared

The infrared spectra of organometallic compounds nicely complement the NMR spectra just as in conventional organic chemistry. While proton NMR spectra are quite informative about the hydrocarbon portion of the organic ligand, the infrared spectra are more useful for the information they provide about the functional groups. In those cases in which CH stretching and bending modes have been reported for organic ligands, the frequency values are quite ordinary. For example, the unique hydrogen of  $(\text{CH}_3)_2\text{CHFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  gives a stretching frequency at  $2930\text{ cm}^{-1}$  (confirmed by deuteration) and the methyl CH's absorb at  $2960$  and  $2850\text{ cm}^{-1}$ . The CH deformation modes are at  $1380(\text{s})$ ,  $1365(\text{s})$ , and  $1315(\text{w})\text{ cm}^{-1}$ , also quite normal values for an isopropyl group (69).

In contrast to the CH vibrations, the C=O stretching frequencies of acyl metal complexes may differ greatly from those of aldehydes or ketones. Values ranging from  $1590\text{ cm}^{-1}$  for  $\text{CH}_3\text{COFe}(\text{CO})(\text{PBU}_3)(\pi\text{-C}_5\text{H}_5)$  to  $1728\text{ cm}^{-1}$  for  $\text{CH}_3\text{COCO}(\text{salen})(\text{H}_2\text{O})$  have been reported (76, 77).<sup>2</sup> Within a given series such as  $\text{CH}_3\text{COM}(\text{CO})_n(\pi\text{-C}_5\text{H}_5)$  or  $\text{CH}_3\text{COMCl}(\text{PEt}_3)_2$ , the heavier metals give rise to lower C=O stretching frequencies (78). The effect of the metal or the other ligands on  $\nu_{\text{CO}}$  is not confined to acyl derivatives. Schrauzer (24) has noted  $\nu_{\text{CO}}$  shifts for the dimethyl-

<sup>2</sup> salen = bis(salicylaldehyde)ethylenediiminato.

glyoxime (DMG) complexes  $\text{CH}_3\text{OCO}(\text{CH}_2)_n\text{Co}(\text{DMG})_2(\text{py})$  which correlate with the acidities of the corresponding carboxylic acids.

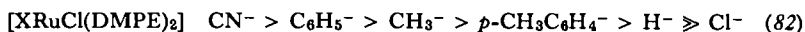
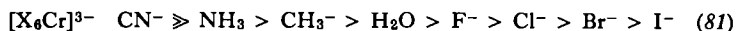
Recent work on low-frequency spectra led to the assignment of C—M stretching and deformation modes for methyl derivatives of ruthenium (13), palladium (18), and platinum (79). Somewhat higher force constants are indicated for  $\text{CH}_3\text{—Pt}$  bonds than for  $\text{CH}_3\text{—Pd}$  bonds in analogous compounds (18). This result is consistent with the observed greater stability of the platinum complexes. The number of C—M stretching frequencies is usually that predicted by group theory. For example, *cis*-( $\text{CH}_3$ )<sub>2</sub>Pt(PMe<sub>3</sub>)<sub>2</sub> gives two strong bands at 508 and 525  $\text{cm}^{-1}$ . The exact value of  $\nu_{\text{C—M}}$  is dependent on the other ligands present in the complexes. In the series *trans*- $\text{CH}_3\text{PtX}(\text{PEt}_3)_2$ ,  $\nu_{\text{C—Pt}}$  decreases with increasing trans effect of the anionic ligand X.

The trans effect correlation also applies to M—X stretching frequencies of anionic ligands trans to an alkyl or aryl ligand (80). Although most organic ligands have high trans effects, the relative strength seems to fall in the series  $\text{H} > \text{C}_6\text{H}_5 > \text{CH}_3$  as judged by  $\nu_{\text{Pt—Cl}}$  in the series *trans*-RPtCl(PEt<sub>3</sub>)<sub>2</sub>.

### 3. Electronic Spectra

In general the ultraviolet and visible spectra of organic derivatives of the transition metals are made up of strong charge-transfer bands and relatively weak (formally forbidden) *d—d* transitions. The energies of the *d—d* transitions such as that from the highest bonding orbital to the lowest antibonding orbital depend on the aggregate field strength of the ligands about the metal atom. The frequencies of these transitions have been compared in series of compounds such as  $[\text{XCo}(\text{CN})_5]^{3-}$  to give a spectrochemical series of the variable ligand X.

Alkyl and aryl groups are moderately strong field ligands as judged by comparison of two series of octahedral complexes. The spectrochemical series derived from the compounds are<sup>3</sup>



Halpern and Maher (33) similarly concluded that  $\text{CH}_3^-$  approaches  $\text{CN}^-$  in ligand field strength in the series  $[\text{XCo}(\text{CN})_5]^{3-}$  but, for the tetrahedral complexes  $\text{XCoCl}(\text{PR}_3)_2$ , the series  $\text{Cl}^- > \text{C}_6\text{Cl}_5^- > \text{CH}_3^- > \text{I}^-$  has been

<sup>3</sup> DMPE = tetramethylethylenediphosphine.

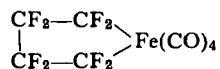
proposed (83). Similarly, in  $\text{XTiCl}_2 \cdot 3$  pyridine compounds,  $\text{Cl} > \text{phenyl} > \text{CH}_3$ . The spectra of phenyl compounds with para substituents show a correlation between wavelength and the Hammett  $\sigma_p$  value for the substituent (84).

In contrast to this interesting comparative data, the electronic spectra of individual organometallic compounds convey little information about the nature of organic ligands. Many of the transitions reflect the gross electronic state of the metal atom rather than specific metal-ligand interactions. Thus, the spectral information available for  $(\text{C}_2\text{H}_5)_2\text{Ni}(\text{bipy})$ ,  $\text{ArPtCl}(\text{PEt}_3)_2$ , and  $[\text{ArV}(\pi\text{-C}_5\text{H}_5)_2]^+$  tell little about the effect of the organic ligands (57, 70, 85).

#### 4. Mass Spectrum

Within the last 10 years, organic chemists have recognized mass spectrometry as an outstandingly useful tool for characterization of new compounds. The application of mass spectrometry to organometallic complexes is even more recent but the results reported to date suggest that the mass spectrum will be equally useful for these compounds.

In one of the earliest applications to an organometallic compound, the mass spectrum of the product from tetrafluoroethylene and  $\text{Fe}_3(\text{CO})_{12}$  established that the formula was  $\text{C}_4\text{F}_8\text{Fe}(\text{CO})_4$  rather than  $\text{C}_4\text{F}_8\text{Fe}(\text{CO})_3$ , as had been reported earlier (86). The fragmentation pattern confirmed that the two  $\text{C}_2\text{F}_4$  ligands had combined with the iron to give a five-membered ring,



The parent mass peak corresponding to the molecular weight of the compound is not always observed. The spectrum of  $(\text{CH}_3)_3\text{NbCl}_2$  shows a strong cluster of peaks at 193, 195, and 197 assignable to the  $[(\text{CH}_3)_2\text{-NbCl}_2]^+$  ion as the highest mass peaks observable at an ionizing voltage of 70 eV. The relative intensities of these peaks correspond to the abundances of the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopes (15). In the mass spectrum of  $\text{C}_6\text{H}_5\text{CH}_2\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ , the parent mass is very weak but a strong peak corresponding to  $[\text{C}_7\text{H}_7\text{FeC}_5\text{H}_5]^+$  occurs. The fragmentation pattern suggests that the  $\text{C}_7\text{H}_7$  ligand in this ion is really a tropylium ring formed by rearrangement of the  $\sigma$ -benzyl ligand (87).

## 5. Electron Spin Resonance

Few ESR spectra have been reported for organic derivatives of transition metals even though several classes of these compounds are paramagnetic and their magnetic moments are known (Section III,B,1). Matsuzaki and Yasukawa (83) used the ESR spectra together with electronic spectra to determine the configuration of  $\text{RCoX}(\text{PhPEt}_2)_2$  compounds. The diaryl derivatives ( $\text{R}=\text{X}=\text{C}_6\text{Cl}_5$ ) are yellow and show broad unsymmetrical ESR peaks. At  $-196^\circ\text{C}$ , the peaks show fine structure ascribed to  $g$  anisotropy in a square-planar structure. In contrast, the green monoaryl derivatives ( $\text{R}=\text{C}_6\text{Cl}_5$  or  $\text{CH}_3$ ,  $\text{X}=\text{Cl}$  or  $\text{I}$ ) give symmetrical peaks with a  $g$  factor close to 2 and appear to be tetrahedral. Pyridine derivatives such as  $(\text{CH}_3)_2\text{Co}(\text{py})_2$  were too unstable to be isolated but gave spectra characteristic of square-planar compounds.

## B. Molecular Properties

### 1. Magnetic Moment

Several paramagnetic aryl derivatives of the first-row transition metals are known and magnetic moments have been reported. Most complexes of the first-row elements have moments close to the "spin-only" values and some organic derivatives follow this rule. For example, aryl derivatives of chromium(III) such as  $p\text{-TolCrCl}_2 \cdot 3$  tetrahydrofuran (88) and  $\text{Li}_3[(\text{C}_6\text{H}_5)_6\text{-Cr}]$  (89) have moments of 3.6–3.9 BM appropriate for the presence of three unpaired electrons. However, compounds such as  $\text{Ar}_2\text{Cr}$  and  $\text{Li}[\text{Ar}_3\text{Cr}]$  which can formally be described as chromium(II) complexes give anomalously low moments, 0.35–0.54 BM (90). The low moments probably result from metal–metal interactions in a complex polynuclear structure.

Chatt and Shaw (91) report abnormally high magnetic moments for  $\text{Ar}_2\text{M}(\text{PR}_3)_2$  compounds of cobalt and iron. *trans*-Dimesitylbis(phenyldiethylphosphine)cobalt, a square-planar Co(II) complex that might be expected to have a moment of about 1.8 BM, corresponding to one unpaired electron, actually gave a value 2.5 BM. However, Figgis and Nyholm (92) reported even higher values for planar complexes of Co(II) with chelate ligands. This phenomenon is ascribed to spin–orbit coupling like that observed in complexes of the heavier transition elements.

### 2. Dipole Moment

Dipole moments are often recorded for organic derivatives of the transition metals. Although this property is characteristic of the molecule as a

whole and tells little about the organic ligand, it is useful in the assignment of molecular geometry. The dipole moments of  $R_2M(PR'_3)_2$  compounds of Fe, Co, Ni, Pd, and Pt have been reported. The Fe, Co, and Ni complexes gave values near zero consistent with trans, square-planar structures (91, 93). In the platinum series, isomers were isolated with dipole moments of about 0 and 5.5–8.4 D corresponding to the trans and cis isomers (43). With  $(CH_3)_2Pd(PEt_3)_2$ , the cis isomer was unstable and gave a value of 4.68 D which slowly decayed to 1.4 D over a period of 6 months, presumably due to isomerization (18). Cis–trans isomerism of octahedral complexes such as  $(CH_3)_2Ru(Ph_2PCH_2CH_2PPh_2)_2$  has also been resolved by dipole moment measurements (13).

Jenkins and Shaw (94) recently observed that cis–trans isomerism of alkylphosphine complexes can be established more easily by analysis of the proton NMR spectra of the P alkyl groups. The spectra of trans isomers reflect very strong P–P coupling but the coupling is much weaker when the phosphorus ligands occupy cis positions on the metal atom.

### 3. Crystal Structure

X-Ray crystallography provides much useful information about the structure of organometallic compounds in the solid state. Churchill and Mason (95) have reviewed recent developments concerning organo–transition metal complexes so we shall not discuss crystallographic results except for two generalizations: structural studies suggest that the C–M bond in most of these complexes is strictly covalent and that the alkyl or aryl ligand has a very strong trans effect.

Although it is often convenient to consider transition metal complexes in terms of crystal-field theory, as in the discussion of electronic spectra (Section III,A,3), it should be recognized that the C–M bond is formed by a *covalent* combination of atomic orbitals. For  $\sigma$ -alkyl and aryl compounds, C–M bond lengths are almost exactly those predicted by addition of the covalent radii for carbon and for the transition metal in the appropriate valence state. In  $C_2H_5Mo(CO)_3(\pi-C_5H_5)$ , the  $\sigma$ -C–Mo bond length is 2.38 Å, the same length calculated for a covalent C–Mo bond (96). In accord with this postulate of covalency, little or no ionic character is reflected in the dipole moments of simple  $\sigma$ -alkyl derivatives. The additive character of C–M bond lengths does not extend to fluoroalkyl or acetylenic derivatives of transition metals, both of which show significant bond shortening. The origin of  $R_F$ –M bond shortening (97) is the subject of



some controversy (Section III,C). In  $(\text{C}_6\text{H}_5\text{C}\equiv\text{C})_2\text{Ni}(\text{PEt}_3)_2$ , the C—Ni bond length is  $1.879 \pm 0.011$  Å compared to a calculated length of 2.08 Å; the shortening was ascribed to  $d_\pi$ - $p_\pi$  multiple bonding analogous to that found in the M—CO bond (98).

In the discussions of NMR and infrared spectra, indirect evidence was cited for a strong trans effect of the alkyl or aryl ligand. The effect is illustrated directly in the crystal structure of  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CrCl}_2 \cdot 3\text{THF}$  (99).<sup>4</sup> The structure is octahedral with two THF ligands cis to the *p*-tolyl group and one trans. The Cr—O bond lengths of the cis ligands are  $2.045 \pm 0.008$  Å and that of the trans ligand is  $2.214 \pm 0.007$  Å. The bond weakening of the trans ether ligand is almost certainly assignable to the inductive effect of the *p*-tolyl group.

### C. Stability

In a general sense, a stable compound is resistant to degradation by heat, oxidation, or hydrolysis. By any criterion, the simple transition metal alkyls (neutral compounds which have only alkyl ligands on the metal atom) are very unstable. Dimethylmanganese, for example, is a spontaneously flammable solid which explodes on impact. Most other simple transition metal alkyls seem to be thermodynamically unstable relative to alkyl radicals and the free metal, although quantitative data are not available.

In contrast to the simple alkyls, some metal complexes bearing other ligands in addition to alkyl or aryl groups are strikingly stable. The bond energy of the C—Pt bond in *trans*-( $\text{C}_6\text{H}_5$ )<sub>2</sub>Pt(PEt<sub>3</sub>)<sub>2</sub> is about 60 kcal/mole (100), roughly equal to that of a C—C bond in an alkane. The stability of most alkyl derivatives is primarily kinetic. The alkyls can react with air or water to give thermodynamically favored products, but the activation energies of these processes are high. The high activation energies may be due to steric hindrance or to the saturation of potential bonding orbitals required in the transition state for the reaction. In this connection, stability is usually associated with an "inert-gas configuration" of the central metal atom. The major exceptions to this rule are  $d_8$  square-planar complexes in which the vacancy is present in an inaccessible orbital directed toward the ligands.

The most general theory of the stabilization of metal alkyls by electronic factors was proposed by Chatt and Shaw (11) and is elaborated by Coates in

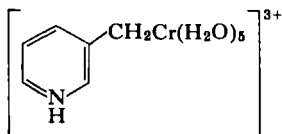
<sup>4</sup> THF = tetrahydrofuran.

"Organometallic Compounds" (1). Briefly, this theory assumes that the initial step in decomposition (either oxidative or thermal) is promotion of an electron from the highest filled orbital to a vacant antibonding orbital. Hence, any factor that increases the energy gap between the filled and vacant orbitals should stabilize the compounds. This effect can be attained either by the presence of strong  $\sigma$ -donor ligands which stabilize bonding orbitals and destabilize antibonding orbitals or by  $\pi$ -acceptor ligands which stabilize the nonbonding  $d$  orbitals of the metal by forming  $\pi$ -bonds.

There are few recognized examples of stabilization by pure  $\sigma$ -donor ligands. Perhaps the most remarkable is the stability of  $[(\text{NH}_3)_5\text{RhH}]^{2+}$ . This complex is stable in aqueous solution in the absence of oxygen and is stable to air in the solid state (101). One may expect a similar stability for the analogous alkyl compound  $[\text{CH}_3\text{Rh}(\text{NH}_3)_5]^{2+}$ . Among similar alkyl derivatives, the alkylchromium compounds



and



seem to be most stable. These ions are stable to water and even show limited oxidative stability in solution. The anionic complexes  $\text{Li}_3\text{Cr}(\text{C}_6\text{H}_5)_6$  (89),  $\text{Li}_2\text{W}(\text{CH}_3)_6$  (102), and  $\text{Li}_2\text{Nb}(\text{C}_6\text{H}_5)_7$  (103) are oxidatively unstable but the very existence of these compounds at room temperature is in remarkable contrast to the instability of the simple alkyl derivatives of these elements. The stability of the anionic complexes is probably due to the absence of vacant potentially bonding orbitals. In this sense they resemble the hydride  $\text{K}_2\text{ReH}_9$ . One might expect that organorhenium anions such as  $[\text{Re}(\text{C}\equiv\text{CC}_6\text{H}_5)_9]^{2-}$  or  $[\text{Re}(\text{C}_6\text{H}_5)_7]^{2-}$  would also be stable.

Many stable alkyl and aryl derivatives of transition metals contain  $\pi$ -acceptor ligands such as CO or  $\text{C}_5\text{H}_5^-$ . Compounds of the types  $\text{RTiCl}(\text{C}_5\text{H}_5)_2$ ,  $\text{RMo}(\text{CO})_3\text{C}_5\text{H}_5$ , and  $\text{RMn}(\text{CO})_5$  are moderately stable to air in the solid state and sometimes in solution. The Group VIII compounds such as  $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$  and  $\text{RCo}(\text{CO})_4$  are less stable than those of Groups VI and VII but are much more stable than the simple alkyl

derivatives. The stability of these compounds can be attributed to the presence of the  $\pi$ -acceptor ligands.

The most stable transition metal alkyls are those of the heavier Group VIII metals that bear tertiary phosphine ligands. The powerful stabilizing effect of a phosphine is probably assignable to a combination of  $\sigma$ -donor and  $\pi$ -acceptor action. The phosphine ligands are moderately strong  $\sigma$ -bases; the  $^{31}\text{P}$  coupling constants in  $(\text{R}_3\text{P})_2\text{PtX}_2$  compounds suggest that phosphines are more effective  $\sigma$ -donors than are amines with respect to transition metals. The  $\pi$ -acceptor effect of phosphorus is probably real, as evidenced by the stability of metal complexes of  $\text{PF}_3$  and  $\text{P}(\text{OPh})_3$ , but it is more difficult to confirm spectroscopically. Pidcock *et al.* (104) have concluded that the strong trans effect of phosphine ligands is almost entirely due to a  $\sigma$ -donor action without invoking a  $\pi$ -effect.

Electron-withdrawing substituents, especially fluoroalkyl groups, stabilize transition metal derivatives. Compounds such as octafluorotetramethylenetetracarbonyl display remarkable thermal and oxidative stability. There has been speculation that these compounds are stabilized by negative hyperconjugation or "no bond" resonance. Spectroscopic evidence (105, 105a) has been cited in favor of resonance structures such as



However, a recent study of highly fluorinated organic compounds indicates that the perfluorocarbon anion is stabilized simply by inductive effects (106). These effects may possibly be adequate to account for the stability of the perfluoroalkyl metal compounds.

Some empirical rules can be used to predict stabilities of  $\sigma$ -alkyl and aryl transition metal complexes. In general, the heavier metals tend to give more stable compounds than the lighter elements if the ligands are the same. The stability sequence for the organic ligand is usually fluoroalkyl > aryl > methyl > ethyl > *n*-propyl > isopropyl. As mentioned earlier, stability is usually associated with a "noble gas" electron configuration for the metal. In the series  $\text{R}_2\text{ML}_2$ , the stability sequence for M seems to be  $\text{Pt} > \text{Pd} \sim \text{Ni} > \text{Co} > \text{Fe}$ ; for R, *o*-Tol > *m*-Tol  $\sim$  *p*-Tol >  $\text{C}_6\text{H}_5$  > alkyl; and, for L,  $\text{R}_3\text{P} > \text{R}_3\text{As} > \text{R}_2\text{S}$ .

## IV REACTIONS

In this section we discuss reactions of organometallic compounds which involve the metal-carbon bond. Although the alkyl or aryl group<sup>5</sup> strongly influences other metal-ligand bonds in these complexes (and vice versa), we wish to stress the systematic character of C—M bond reactions. These generally fall in two classes:

*Cleavage*, in which the alkyl or aryl group is lost from the metal complex, usually as an alkane or arene.

*Insertion*, in which another reagent is "inserted" into the C—M bond, for example, the insertion of CO to give an acyl metal compound.  $\sigma$ - $\pi$  Rearrangements, homogeneous catalysis, and enzymatic reactions often combine insertion and cleavage steps and are discussed separately.

### A. Cleavage Reactions

#### 1. Protic Solvents and Acids

The most general reaction of organometallic compounds is cleavage by a proton source.



In many instances, water is sufficiently acidic to cleave alkyl and aryl transition metal compounds. However, many of these compounds are hydrophobic or insoluble in water and hydrolyze so slowly that the reaction is not detected in a test tube experiment. For example, methylchlorobis( $\pi$ -cyclopentadienyl)titanium is reported to be stable to cold water (107) but hydrolyzes rapidly in warm water. Few rate studies have been done in mutual solvents for water and organometallics but hydrolysis rates seem to vary by many orders of magnitude. The effect of hydrogen ion concentration has also received little attention but qualitative observations indicate that hydrolysis proceeds faster in acidic solutions.

Nearly all alkyl and aryl transition metal compounds are cleaved by hydrogen halides. Even arylplatinum complexes stabilized by phosphine ligands are rapidly cleaved by hydrogen chloride in methanol or benzene. The reaction

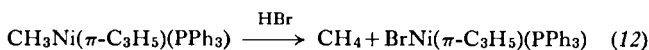
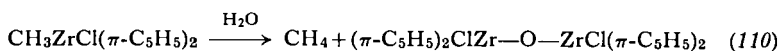


<sup>5</sup> The alkyl and aryl groups are strongly *trans*-activating, i.e. these groups labilize a *trans* ligand in an octahedral or square planar complex.

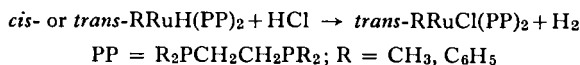
has been carefully studied and shows a simple first-order dependence on hydrogen ion concentration and on substrate concentration (108). The mechanism suggested for this particular reaction involves a rapid, reversible protonation of the platinum followed by a slow elimination reaction with loss of benzene. Doubtless, other mechanisms such as protonation of the carbon atom of the C—M bond operate in other situations such as cleavages of "coordinately saturated" compounds.

Methanol and ethanol usually solvolyze the carbon-metal bond less rapidly than water in homogeneous solution. However, because most qualitative observations involve treatment of the organometallic compound with the neat reagent, there are many reports of more rapid cleavage of R—M bonds by alcohol than by water. For example, the solvolysis of diethyl(2,2-bipyridine)nickel to give ethane is reported to be faster in ethanol than in water at room temperature (70). Similarly,  $(C_6H_5)_2Ti(\pi-C_5H_5)_2$  is reported to be stable to water but reacts with hot alcohols to give benzene (109).

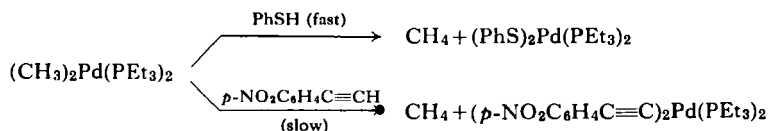
In solvolyses of aryl- or alkylbis( $\pi$ -cyclopentadienyl)titanium compounds, the  $\pi$ -cyclopentadienyl ligand is more stable toward solvolysis than is the  $\sigma$ -alkyl ligand. This trend in stability is general although perhaps not universal. Other examples, including one involving discrimination between a  $\pi$ -allyl and a  $\sigma$ -alkyl group, are



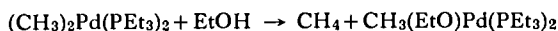
In one compound which contains both hydride and alkyl ligands, H is cleaved in preference to R (13).



Other protonic reagents also cleave alkyl metal compounds. Calvin and Coates (18) report that benzenethiol and even *p*-nitrophenylacetylene cleave a dimethylpalladium compound.



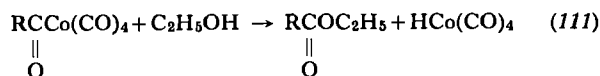
This compound also reacts readily with ethanol. The first step is simple ethanolysis of one methyl group.



The second stage of the reaction is slower and more complex. In addition to methane, some ethane and ethylene are evolved. Metallic palladium and acetaldehyde are also formed, reminiscent of the Smidt reaction (Section IV,D). It was suggested that these products arise from free radical decomposition of  $\text{CH}_3(\text{EtO})\text{Pd}(\text{PEt}_3)_2$ . Addition of styrene to the reaction mixture gave polystyrene and suppressed the formation of ethane and ethylene in accord with this postulate.

As typified by the ethanolysis of  $(\text{CH}_3)_2\text{Pd}(\text{PEt}_3)_2$ , many solvolyses of metal-carbon bonds are found to be quite complex when studied in detail. Even the generalization that the C—M bond hydrolyzes to give alkane and metal ion is not universally valid. Schrauzer and Windgassen (23) found that a methylcobalt compound with dimethylglyoxime ligands gave methane and methyl chloride in a 3:1 ratio on treatment with hot concentrated hydrochloric acid. Traces of ethane also formed, apparently by thermal decomposition with formation of methyl radicals. Warm concentrated KOH solution decomposed this complex with formation of methane.

Water and alcohols cleave some acyl-metal bonds to give carboxylic acid derivatives and a metal hydride, another example of an "inverse" cleavage. This reaction has been studied with acylcobalt carbonyl derivatives such as



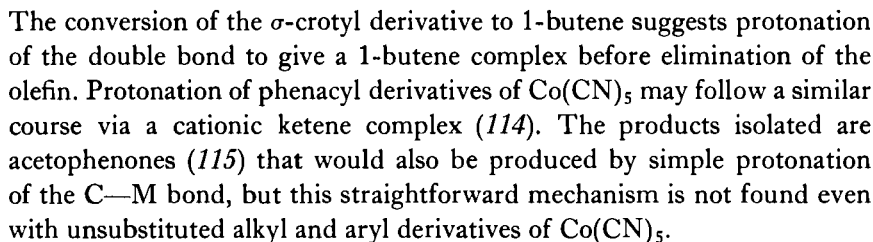
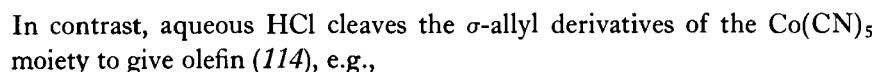
The cleavage is a crucial step in the catalytic carboxylation of olefins because the formation of  $\text{HCo}(\text{CO})_4$  permits continuation of the catalyst cycle. Olefin addition gives  $\text{RCo}(\text{CO})_4$  which is then carbonylated to the acyl compound.

The reactivity of the carbon-metal bond depends on the other ligands in the organometallic compound. The stepwise cleavage of a *trans*-diphenyl-platinum compound provides an interesting example of the *trans* effect (43).



The first step proceeds rapidly at 0° C but, even with excess HCl present, the second phenyl group is cleaved slowly and the monophenyl derivative

The cleavage of  $\sigma$ -allyl groups by protonic acids is often more complex than removal of simple alkyl groups. Green (52, 112, 113) has shown that  $\sigma$ -allyl derivatives of Fe, Mn, Mo, and W are protonated to cationic propylene complexes by anhydrous HCl.



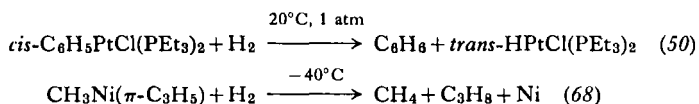
The acid cleavage of simple  $[\text{RCo}(\text{CN})_5]^{3-}$  derivatives is complex because cyano ligands on a metal ion are also susceptible to protonation. The protonated CN becomes an isonitrile-type ligand and undergoes an insertion reaction with the alkyl ligand to give, ultimately, a nitrile or a carboxylic acid (114, 116).

The hydrolyses of tris( $\sigma$ -aryl)chromium compounds are very complex. As discussed in Section IV,C, rearrangements occur to give  $\pi$ -arene-chromium(0) compounds in addition to arenes and biaryls (117).

## 2. Hydrogen and Reducing Agents

The reductive cleavage of the carbon-metal bond has received much less attention than hydrolytic and oxidative cleavages, presumably because we usually work in a moist, oxidizing atmosphere. However, it is important in many industrial operations such as the "oxo process" because the cleavage generates an H—M bond which can be reconverted to a C—M bond by olefin insertion.

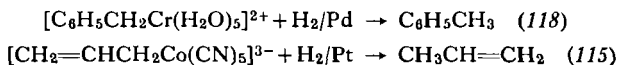
Molecular hydrogen sometimes cleaves the C—M bond remarkably easily, as in the reactions



In the latter reaction, metallic nickel may catalyze hydrogenation of propylene to propane. Traces of ethane and butane found as by-products probably arise from methyl free radical reactions.

The ease of hydrogenolysis depends on reaction conditions and structural factors. Diphenylmanganese is stable to hydrogen in toluene (20° C, 1 atm, 24 hr) but rapidly decomposes to benzene and manganese under comparable conditions in tetrahydrofuran (107).  $\text{CH}_3\text{TiCl}(\pi\text{-C}_5\text{H}_5)_2$  is reported to be stable to hydrogen at 20° C, but  $(\text{CH}_3)_2\text{Ti}(\pi\text{-C}_5\text{H}_5)_2$  gives methane and a dark green solid tentatively identified as titanocene (107).

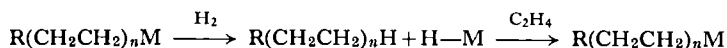
Conventional hydrogenation catalysts such as palladium and platinum also catalyze hydrogenolysis of the C—M bond.



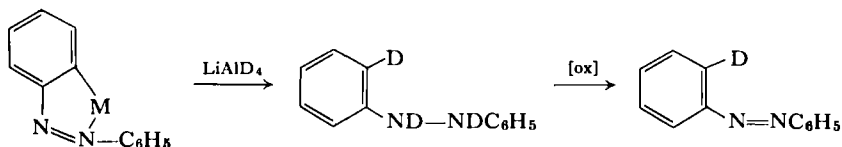
There is some evidence that  $[\text{HCo}(\text{CN})_5]^{3-}$  acts as a homogeneous catalyst in the hydrogenolysis of  $\sigma$ -alkyl compounds of the type  $[\text{RCo}(\text{CN})_5]^{3-}$  (115).



As discussed in Section IV,D (Catalysis), the hydrogenolysis reaction is a key step in catalytic hydrogenation and hydrocarbonylation of olefins. It finds more direct application as a "chain transfer" agent in the coordination polymerization of olefins (107). Traces of hydrogen are added with the olefin feedstock to limit the average molecular weight of the polyolefin. Periodic cleavage of a polymeric ligand from the polymerization site terminates the growth of one chain and initiates the growth of another.



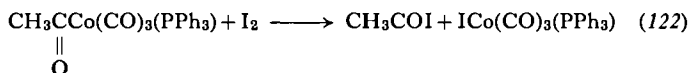
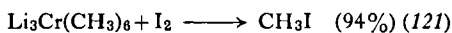
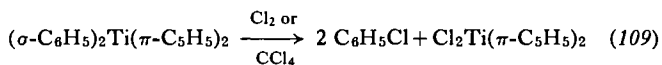
Other reducing agents such as  $\text{NaBH}_4$  and  $\text{LiAlH}_4$  also open carbon-metal bonds. One elegant application was in the structure determination of azobenzene complexes of nickel, palladium, and platinum (119, 120).



Alkylcobalt(III) compounds have been reduced to alkanes and cobalt(II) complexes by  $\text{NaBH}_4$ , by catalytic hydrogenation, and by electrolysis. A polarographic wave at  $-1.7$  V (vs.  $\text{Ag}/\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$ ) was assigned to  $\text{C}-\text{Co}$  bond cleavage (23).

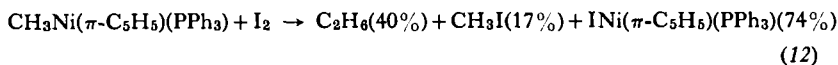
### 3. Halogens and Alkyl Halides

The reaction of a halogen with an organometallic compound to give an alkyl or aryl halide is often used to diagnose the presence of a  $\text{C}-\text{M}$  bond. Reactive alkyl halides such as  $\text{CCl}_4$  may also cleave the  $\text{C}-\text{M}$  bond. Some examples are

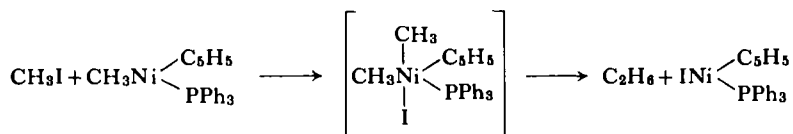


The reaction seems to be quite general, but a few alkylplatinum(IV) complexes and some perfluoroalkyliron compounds seem to be immune to halogen at room temperature. 1-Naphthyl $\text{NiBr}(\text{PhPEt}_2)_2$  apparently undergoes bromination of the aromatic ring with little  $\text{C}-\text{M}$  bond cleavage (93).

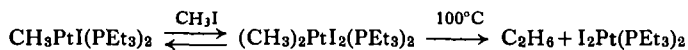
Although the halogen cleavage of the C—M bond is superficially straightforward, very little is known about the mechanism. Sometimes coupling products are formed in addition to alkyl or aryl halides.



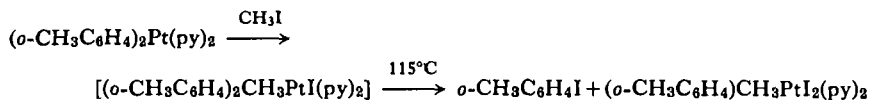
In the latter reaction, the ethane may arise as a secondary product from methyl iodide by the sequence:



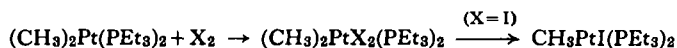
The intermediate in such an addition–elimination sequence has been isolated in the reaction of a square-planar platinum(II) complex with methyl iodide (11).



A similar intermediate may be involved in an exchange of a methyl group for an *o*-tolyl group in a platinum(II) complex (123).



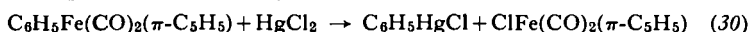
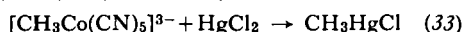
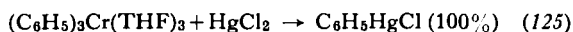
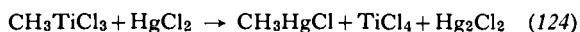
Halogens add to platinum(II) complexes similarly (11).



If the halogen is chlorine, the Pt(IV) adduct is stable. Diarylplatinum complexes of this type give stable adducts with either chlorine or iodine (43).

#### 4. Metal Halides

The reaction of  $\text{HgCl}_2$  with an organometallic compound is also widely used to test for the presence of a C—M bond to give a stable organomercuric chloride. As shown by the examples below, the reaction is quite general and yields are often good but little is known about the mechanism of the transfer reaction.



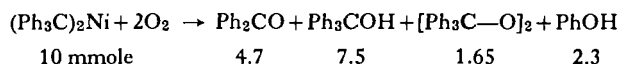
Attempts to transfer alkyl or aryl groups to metals other than mercury have been less successful. The most remarkable of these is the reported transfer of a methyl group from *cis*-(CH<sub>3</sub>)<sub>2</sub>Pt(PEt<sub>3</sub>)<sub>2</sub> to MgI<sub>2</sub> to give a methyl Grignard reagent (11).

## 5. Oxygen

Many organometallic compounds react with oxygen (diphenylmanganese explodes in air!), but these oxidations have not been studied carefully. The reaction paths are quite complex and diverse.

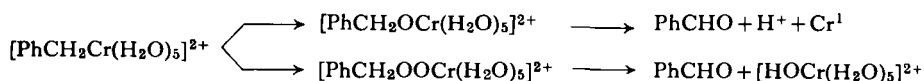
Free radical processes are common, as indicated by the formation of biphenyl in the oxidations of many phenylmetal compounds. Oxygen reacts with C<sub>6</sub>H<sub>5</sub>TiCl<sub>3</sub> (126) and with Li<sub>3</sub>Cr(C<sub>6</sub>H<sub>5</sub>)<sub>6</sub> (89) in benzene solution to give substantial amounts of biphenyl. In CCl<sub>4</sub> solution, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Ti(π-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> gives biphenyl, chlorobenzene, phosgene, and Cl<sub>2</sub>Ti(π-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>. However, in isopropanol, the major organic products are phenol and acetone (109, 127).

An "insertion" of an O<sub>2</sub> molecule appears to occur in the oxidation of ditritylnickel. Treatment of this compound with oxygen at 20° C in solution leads to absorption of 2 moles of O<sub>2</sub>, presumably to give bis(tritylperoxy)-nickel which decomposes to give the following products (42):



A single oxygen atom appears to insert into the C—Ti bond of CH<sub>3</sub>TiCl<sub>3</sub> to give initially CH<sub>3</sub>OTiCl<sub>3</sub>, which disproportionates to (CH<sub>3</sub>O)<sub>2</sub>TiCl<sub>2</sub> and TiCl<sub>4</sub> (127).

The oxidation of some alkyl derivatives to aldehydes may also occur by insertion. Either a one- or two-atom insertion could be involved, as illustrated in the oxidation of benzylchromium complex to benzaldehyde (118).



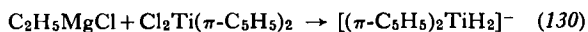
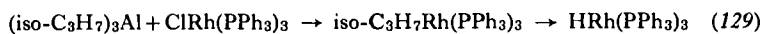
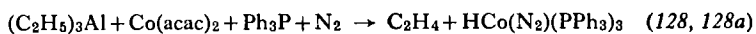
Alkylcobaloxime complexes give aldehydes on photolysis in air (23). Since these same complexes give alkyl radical products on photolysis in vacuum, the "insertion" process may have a free radical mechanism.

## 6. Olefin Elimination

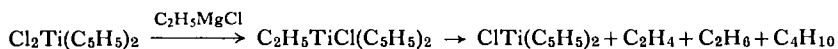
Several alkyl transition metal compounds decompose by olefin elimination with transfer of hydrogen from a  $\beta$ -carbon to the metal atom, as in



This process is simply the reverse of the olefin "insertion" reaction by which several alkyl metal compounds have been made (Section II,D). The elimination of ethylene from the ethylplatinum compound can be reversed under ethylene pressure (50). The elimination reaction appears to be involved in the formation of three extraordinarily reactive transition metal hydrides.



This latter reaction is typical of mixed decomposition processes in which olefin elimination and homolytic cleavage of the C—M bond occur simultaneously or in quick succession. The following stages may be involved:



The ethylchloro compound produced in the first alkylation is moderately stable when pure but the diethyl Ti(IV) compound decomposes readily to give a Ti(III) compound and products derived from the ethyl radical. Olefin elimination from the ethyltitanium(III) complex presumably gives a hydride that can react further to give the observed dihydrido complex.

Other alkylcobalt and alkyltitanium compounds, especially those with branched alkyl substituents, also decompose by olefin elimination. The isobutyl complex,  $[(\text{CH}_3)_2\text{CHCH}_2\text{Co}(\text{CN})_5]^{3-}$ , slowly loses isobutene at room temperature (115). The unique stability of methyl derivatives of the transition metals relative to other alkyl derivatives is partly due to the absence of a  $\beta$ -hydrogen atom which can be transferred to the metal. The

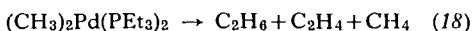
elimination of acrylonitrile from  $\beta$ -cyanoethylcobalt compounds is catalyzed by bases which presumably assist in the removal of the  $\beta$ -hydrogen (24).

### 7. Homolytic Cleavages

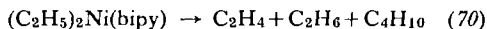
Homolytic cleavage of the C—M bond is the most common process for thermal or photolytic decomposition of alkyl and aryl derivatives of the transition metals. In terms of a molecular orbital scheme, the process involves transfer of an electron from a bonding orbital to a C—M antibonding orbital. Electronic factors which broaden the energy gap between these orbitals should stabilize the compound toward homolytic decomposition.

In practice, decomposition temperatures of alkyl and aryl metal compounds vary widely. Unstabilized metal alkyls such as dimethylnickel decompose rapidly at  $-50^\circ\text{C}$ . On the other hand, compounds such as *trans*-( $\text{C}_6\text{H}_5$ )<sub>2</sub>Pt(PEt<sub>3</sub>)<sub>2</sub> are stable to  $180^\circ$ – $200^\circ\text{C}$  (43). The stability of this particular compound is presumably due to several factors. These include the high energy of the phenyl radical, the broad energy spread between orbitals of a third-row transition element, and the  $\pi$ -bonding effect of the phosphine ligand which stabilizes the electrons in otherwise nonbonding orbitals (Section III,C).

Free radical mechanisms have been inferred from product distributions in many pyrolyses and photolyses of alkyl transition metal compounds. For example, phenyltitanium(IV) alkoxides decompose at  $80^\circ\text{C}$  to give Ti(III) alkoxides, benzene, and biphenyl. The presence of phenyl radical was supported by the fact that  $\text{C}_6\text{H}_5\text{Ti}(\text{OBu})_3$  polymerized styrene at a rate comparable to the benzoyl peroxide-initiated polymerization (131). The formation of coupling products, as in the following reactions, has been taken to indicate a radical mechanism.



However, as indicated in Section IV,A,8 below, the latter reaction may actually be a displacement. The formation of nearly equal proportions of olefin and alkane in the decomposition of an alkyl derivative also suggests alkyl radical intermediates.



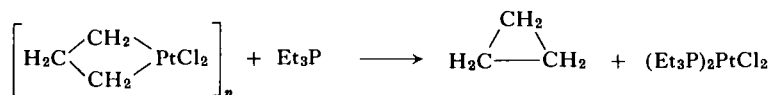
Caution must be used in interpretation of mechanism from product distribution. The thermolysis or photolysis of  $\text{C}_2\text{H}_5\text{TiCl}_3$  gives ethane and

ethylene in a ratio that is not unreasonable for an ethyl radical decomposition. However, decomposition in the presence of cumene gives no cumyl radical (133). Similarly, decomposition of  $\text{CH}_3\text{TiCl}_3$  in cyclohexane- $d_{12}$  gives  $\text{CH}_4$  with no deuterium abstraction from the solvent. Photolysis of  $\text{CD}_3\text{—TiCl}_3$  in *n*-heptane gives  $\text{CD}_4$  and a series of perdeuteroalkanes up to  $\text{C}_9\text{D}_{20}$ . The mechanism of this decomposition is unknown but it is almost certainly bimolecular (133).

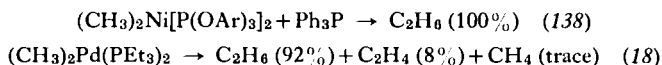
Homolytic cleavage and olefin elimination often occur simultaneously, as with the alkyltitanium discussed in Section IV,A,6. In that example, as in many others, the catalysis of decomposition by impurities complicates the mechanism. A trace of  $\text{TiCl}_4$  catalyzes the apparent homolytic cleavage of the organic groups of  $(\text{CH}_3)_4\text{Ti}$  (134, 134a),  $\text{CH}_3\text{TiCl}_3$  (133, 134, 134a), and  $\text{C}_6\text{H}_5\text{Ti}(\text{O-iso-C}_3\text{H}_7)_3$  (135).

### 8. Alkyl Displacement

Nucleophiles sometimes cleave  $\text{C—M}$  bonds of alkyl derivatives of transition metals. The first such cleavage to be reported was the displacement of cyclopropane from trimethyleneplatinum derivatives by phosphines or by cyanide ion (136, 137), e.g.,

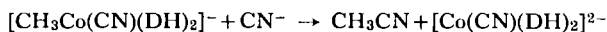


A similar reaction is probably involved in the displacement of ethane from dimethylnickel and -palladium complexes.



Although no nucleophile was added in the palladium reaction, a small amount of free radical decomposition would give enough triethylphosphine to initiate the displacement. The trace of methane may be a measure of the extent of simple radical decomposition.

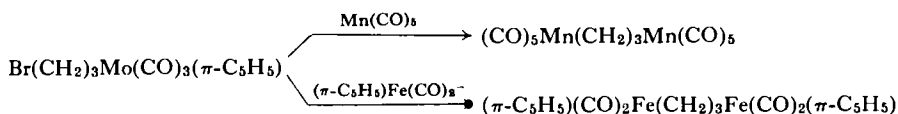
Strongly nucleophilic anions such as cyanide, mercaptide, and  $\text{CH}_3\text{NC}_6\text{H}_5^-$  displace alkyl groups from alkylcobalt(III) complexes of dimethylglyoxime  $[(\text{DH}_2)]$  in a reductive process (23).



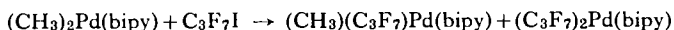
The corresponding cobalt(II) anion can also displace an alkyl group, apparently as a carbanion, since the product in water is methane (23).



Displacement of an alkyl group by a nucleophilic transition metal ion is also seen in the reactions (139)



The replacement of one alkyl or aryl group by another has been discussed in Section IV,A,3. This reaction has been used for the preparation of fluoroalkyl compounds (140).



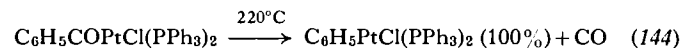
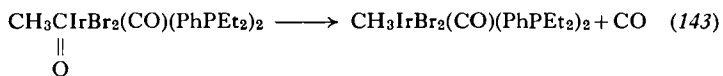
## B. Insertion Reactions

In this section, the term "insertion" is used to designate a reaction in which a C—M bond is broken and rejoined with introduction of a reagent molecule. No mechanistic implications are intended because, as described below, there are experimental indications that "alkyl migration" might be a more accurate descriptive term.

The subject of insertion reactions was reviewed by Heck (141) and by Lappert (142). Our understanding of the carbonylation reaction has greatly improved and insertions of the SO<sub>2</sub> molecule have been discovered.

### 1. Carbonylation

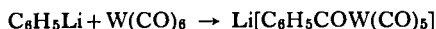
The insertion of carbon monoxide into a C—M bond is a common reaction for alkyl derivatives of the late transition elements. It has been reported for Mo, Mn, Fe, Co, Ni, Pd, and Pt compounds. The insertion of CO into the C—Co bond of cobalt carbonyl derivatives is a key step in the "oxo" reaction and catalytic carboxylation processes (see Section IV,D). The CO insertion reaction is frequently reversible but sometimes only the reverse reaction, CO elimination, is known, e.g.,



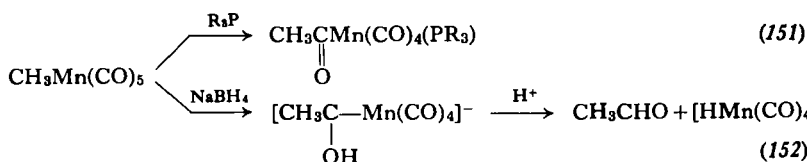
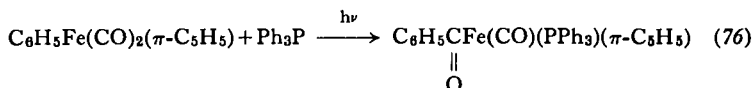




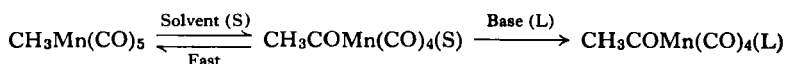
as a "methyl migration" rather than a "carbonyl insertion." This intramolecular attack on a coordinated CO resembles the known intermolecular attack of a carbanion on a coordinated CO (150).



A precoordinated carbon monoxide is sometimes inserted into a C—M bond by treatment of the complex with a donor ligand such as a phosphine, an amine, or even a borohydride ion.



This base-induced CO insertion is more complex from a kinetic viewpoint than the simple carbonylation of  $\text{CH}_3\text{Mn}(\text{CO})_5$ . Although in non-polar solvents such as hexane and mesitylene, the rate of carbonylation is dependent on both  $\text{CH}_3\text{Mn}(\text{CO})_5$  and base [ $\text{C}_6\text{H}_{11}\text{NH}_2$ ,  $\text{Ph}_3\text{P}$ ,  $(\text{PhO})_3\text{P}$ ] concentrations, the rate depends only on  $\text{CH}_3\text{Mn}(\text{CO})_5$  concentration in polar solvents (151). This result suggests the operation of two competitive mechanisms: (1) a bimolecular reaction like that proposed for the CO reaction, and (2) a solvent-assisted sequence such as

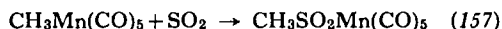
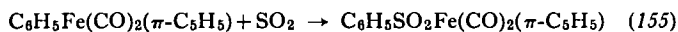


However, the second mechanism alone may account for all the experimental observations if appropriate assumptions are made concerning the rates of the two steps in this sequence (151). The stereochemistry of the products in the triphenylphosphine-induced carbonylation is also strongly dependent on reactants and reaction conditions. Triphenylphosphine and -arsine gives largely *trans*- $\text{CH}_3\text{COMn}(\text{CO})_4(\text{L})$  as the initial products but some amines give exclusively *cis* products (153).

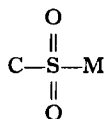
## 2. Sulfur Dioxide Insertion

The insertion of  $\text{SO}_2$  into a C—M bond analogous to the carbonylation reaction was first reported (154) in 1964, although the reaction had been

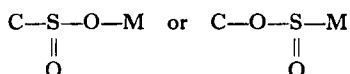
attempted earlier with  $[\text{RCr}(\text{H}_2\text{O})_5]^{2+}$  compounds (118). In a survey of the reaction of  $\text{SO}_2$  with alkyl and aryl transition metal derivatives, Wojcicki and co-workers (155–157) found facile insertion with Mo, Mn, Re, and Fe compounds. In general, insertion occurred when the organometallic compound was dissolved in liquid  $\text{SO}_2$  at  $-40^\circ$  to  $-75^\circ \text{C}$ .



In all the reported examples, the product had the sulfone-type structure,

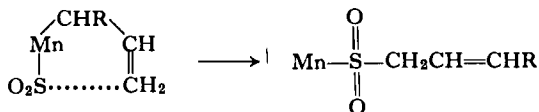


rather than



The order of reactivity of alkyl or aryl groups toward insertion in the iron series (155) is  $\text{CH}_3 \sim \text{C}_2\text{H}_5 \gg (\text{CH}_2)_3 > \text{C}_6\text{H}_5 \sim \text{CH}_2\text{C}_6\text{H}_5 \gg \text{C}_6\text{F}_5$ , a somewhat different sequence than that reported for carbonylation of  $\text{RMn}(\text{CO})_5$ .

Sulfur dioxide reacts with  $\sigma$ -allylmanganese pentacarbonyl more rapidly than with the simple alkyl derivatives. This ease of reaction may be due to a cyclic mechanism peculiar to the allyl ligand.



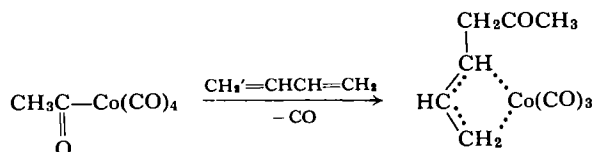
Experimentally, a methyl group on the 1-carbon of the original allyl compound was found on the 3-carbon of the allylsulfinate ligand (158). The postulated mechanism requires precoordination of the  $\text{SO}_2$  to the metal atom. A similar precoordination followed by an alkyl migration from Mn to S could also be involved in the insertion reaction with simple alkyls. In these experiments, which could involve competition between CO insertion and  $\text{SO}_2$  insertion, only the latter is observed.

S-Sulfinate derivatives of Ir, Pt, and Pd that are not accessible from  $\text{SO}_2$  insertion have been prepared by oxidative addition reactions of alkyl-

and arylsulfonyl chlorides (44, 56, 159). The iridium and platinum arylsulfonates lose  $\text{SO}_2$  at  $110^\circ\text{C}$  in a reversal of the hypothetical insertion reaction (44, 56) (Section II,E).

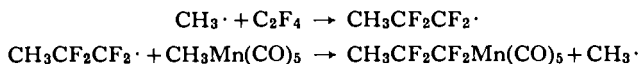
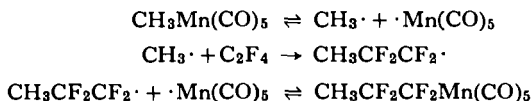
### 3. Insertions of Other Ligands

The insertion of an olefin into a  $\text{C—M}$  bond is a critical step in some olefin dimerization and polymerization reactions (Section IV,D), but studies of this reaction have not been very fruitful. The insertion of isobutylene into the  $\text{C—Ti}$  bond of  $\text{CH}_3\text{TiCl}_3$  to give a neopentyl derivative is one of the few straightforward examples of this reaction (133). Olefin, diene, and acetylene insertion in acylcobalt compounds have been reported by Heck in an elegant series of papers summarized in his review of this area (3). These insertions are often quite complex, as illustrated by the butadiene insertion.



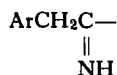
The analogous reaction of butadiene with  $\text{C}_6\text{H}_5\text{Mn(CO)}_5$  gives a benzoyl- $\pi$ -butenyl $\text{Mn(CO)}_4$  complex, presumably by insertion of the diene into the  $\text{C—Mn}$  bond of an intermediate  $\text{C}_6\text{H}_5\text{COMn(CO)}_4$  complex. However, isomerization appears to follow insertion because the acyl group is found on the 1-carbon of the  $\pi$ -butenyl ligand rather than on the 4-carbon as in the cobalt example (160).

Insertions of fluoroolefins, especially tetrafluoroethylene, into the  $\text{C—M}$  bond may occur by different processes. The reaction of  $\text{R—Mn(CO)}_5$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ ) with  $\text{C}_2\text{F}_4$  leads to insertion of a single  $\text{C}_2\text{F}_4$  to give  $\text{RCF}_2\text{CF}_2\text{Mn(CO)}_5$  (161). The reaction with  $\text{CH}_3\text{Re(CO)}_5$  gives the corresponding product,  $\text{CH}_3\text{CF}_2\text{CF}_2\text{Re(CO)}_5$ , together with  $\text{CH}_3(\text{CF}_2)_4\text{Re(CO)}_5$  and polytetrafluoroethylene (162). The predominance of the monoinsertion product suggests that  $\text{C}_2\text{F}_4$  inserts into the alkyl-metal bond more easily than into a fluoroalkyl-metal bond. The catalysis of these reactions by ultraviolet light indicates a free radical process which need not involve precoordination of the fluoroolefin to the metal atom. Two possible processes are the following:

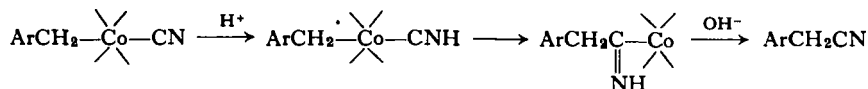
*Radical Chain Sequence**Stoichiometric Cleavage*

Determination of the quantum yield in this reaction should distinguish between these two mechanisms. An alternate mechanism involving photolytic dissociation of CO and precoordination of  $\text{C}_2\text{F}_4$  seems less likely because of the low coordination tendency of this olefin. Many other reactions of alkyl transition metal compounds such as thermal decomposition probably involve radical intermediates but this has not been demonstrated.

Although isonitriles are formally analogous to carbon monoxide and form similar metal complexes, no insertions of  $\text{RN}\equiv\text{C}$  into a  $\text{C}-\text{M}$  bond of a transition compound have been reported (except perhaps in the nitro-genase enzyme, Section IV,E). Hydrogen isocyanide does insert into the  $\text{C}-\text{Co}$  bond of  $[\text{ArCH}_2\text{Co}(\text{CN})_5]^{3-}$  complexes. In the hydrolysis of the 4-pyridiomethyl complex (25%  $\text{H}_2\text{SO}_4$ ,  $33^\circ\text{C}$ ), a rapid change in the proton resonance spectrum and in the electronic spectrum corresponds to the insertion of a protonated cyanide ligand into the  $\text{C}-\text{Co}$  bond. This step is followed by a slow spectral change due to hydrolysis of the



ligand formed by the insertion reaction. The normal product is 4-pyridio-acetic acid but, if base is added after the first spectral change, 4-pyridine-acetonitrile is isolated (116). A similar sequence is noted when the aryl group is phenyl (114).



Some reactions of alkyl and aryl transition metal compounds are formally analogous to those of nontransition metal compounds such as Grignard reagents, but the analogy is very weak. In spite of many attempts, no

successful insertion of carbon dioxide has been reported with a transition metal compound. Similarly, the insertion of ketone into the C—M bond is usually unsuccessful. An exception is the reaction of  $\text{C}_6\text{H}_5\text{Ti}(\text{O-iso-Pr})_3$  with benzophenone. Triphenylcarbinol forms in 19% yield after hydrolysis (131).

### C. Conversion to $\pi$ -Complexes

#### 1. Allyl and Benzyl Complexes

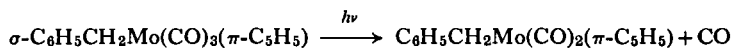
The allyl ligand can be bound to a metal atom either through a simple *sigma* bond or through a combination of the  $\sigma$ -bond and a  $\pi$ -bond involving the olefinic double bond of the ligand. In the presence of easily displaceable ligands such as CO, an equilibrium between the two forms may exist in solution.



In the  $(\sigma + \pi)$ -bond form in which the “ $\pi$ -allyl” ligand formally occupies two sites on the metal atom, the two formal bonds are delocalized and the structure is usually represented as shown for  $\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_4$ . In this symmetrical complex, the terminal carbons of the  $\pi$ -allyl ligand are indistinguishable. However, if either the allyl ligand or the metal is unsymmetrically substituted, the terminal carbons become nonequivalent. This nonequivalence perturbs in the spectral properties and the C—M bond lengths of the complex. The chemistry of the  $\pi$ -allyl compounds has been reviewed by Green and Nagy (9) and Fischer and Werner (10).

Thermal decarbonylation to the  $\pi$ -allyl compound has been observed with  $\sigma$ -allyl derivatives of  $\text{Co}(\text{CO})_4$ ,  $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2$ , and  $\text{C}_5\text{H}_5\text{M}(\text{CO})_3$  (M = Cr, Mo, W). Other ligands displaced by the olefin function of the allyl group are dimethyl sulfoxide in  $\sigma\text{-C}_3\text{H}_5\text{PdCl}(\text{Me}_2\text{SO})_2$  (163) and cyanide ion in  $[\sigma\text{-C}_3\text{H}_5\text{Co}(\text{CN})_5]^{3-}$  (115).

The benzyl ligand has a similar potential for delocalized bonding because it possesses a  $\sigma$ -bond function and the  $\pi$ -system of the aromatic ring. Indeed, King and Fronzaglia (164) observed



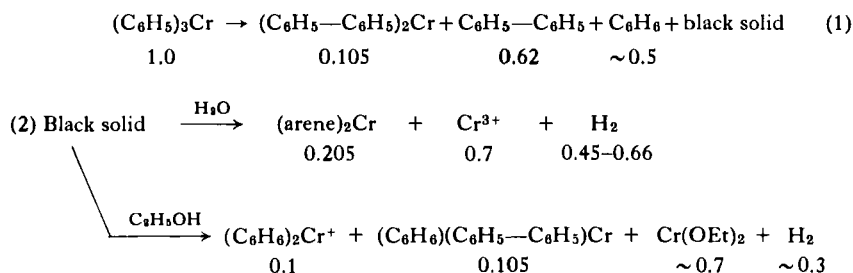
The exact bonding of the  $\pi$ -benzyl ligand is unknown but, on cooling to  $-30^\circ\text{C}$ , the proton NMR spectrum shows nonequivalence of the methylene protons.

The benzyl group also can give  $\pi$ -arene complexes like those described in Section IV,C,2. Tri- $\sigma$ -benzylchromium tetrahydrofuranate, formed from  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$  and  $\text{CrCl}_3 \cdot 3\text{THF}$  at  $-78^\circ\text{C}$ , is converted to the  $\pi$ -toluene- $\pi$ -2-benzyltoluenechromium(I) cation on hydrolysis (132).

## 2. Aryl Ligands

Many  $\sigma$ -aryl derivatives of chromium decompose thermally or rearrange on hydrolysis to give bis( $\pi$ -arene)chromium(0) compounds. Most of these transformations are exceedingly complex and a multitude of products are formed.

In the most thorough study of this reaction, Hähle and Stolze (165) determined the products from a two-step decomposition of triphenylchromium tris(tetrahydrofuranate). In the first step, the complex was allowed to stand in benzene for 2–3 days. Soluble products were extracted at this point and, in the second step, the insoluble black residue was hydrolyzed or ethanolized. The approximate stoichiometries (based on one mole of  $\text{Ph}_3\text{Cr} \cdot 3\text{THF}$ ) are



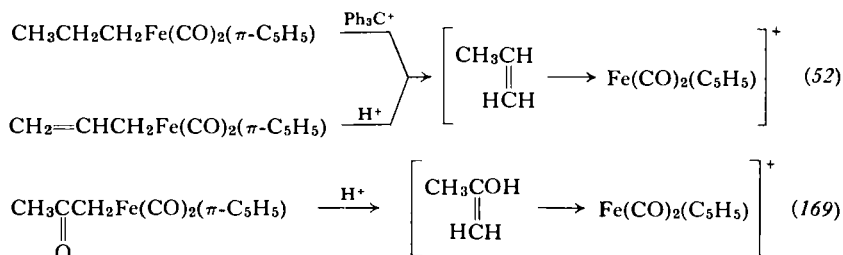
The thermal coupling of phenyl groups may occur without complete separation from the chromium atom, with the result that half of the coordinated arenes are biphenyls. The benzene probably forms by abstraction of hydrogen atoms from solvent by free phenyl radicals. The stoichiometry of the hydrolysis suggests that the black residue is a mixture of chromium(I) compounds containing both  $\sigma$ -phenyl and  $\pi$ -arene ligands. Deuteration studies seem to eliminate benzyne as a significant intermediate.

The transformation of  $\sigma$ -aryl to  $\pi$ -arene chromium complexes does not occur readily with bulky aryl ligands such as mesityl and 1-naphthyl (166).

Both dimesitylchromium(II) (166) and trimesitylchromium(III) (167) (isolated as tetrahydrofuranates) undergo simple hydrolysis to mesitylene and chromium salts without formation of the  $\pi$ -mesitylene complex. Pyrolysis of the  $\sigma$ -mesityl compounds leads to complete decomposition. Electron-withdrawing substituents (e.g., halogen) that destabilize the  $\pi$ -complexes also prevent the  $\sigma$ -aryl to  $\pi$ -arene conversion (168).

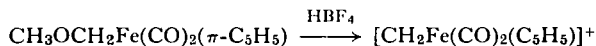
### 3. Olefin and Carbene $\pi$ -Complexes

Several  $\sigma$ -alkyl complexes have been converted to cationic olefin  $\pi$ -complexes by hydride abstraction or, in the case of functionally substituted alkyls, by proton addition to the ligand.



Green has reported similar protonations of  $\sigma$ -allyl complexes of  $\text{C}_5\text{H}_5\text{M}(\text{CO})_3$  ( $\text{M} = \text{Mo}, \text{W}$ ) and of  $\text{Mn}(\text{CO})_5$  (9). Protonation of a cyanomethyl complex,  $\text{NCCH}_2\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ , gives  $[(\pi\text{-HN}=\text{C}=\text{CH}_2)\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)]^+$  (170). Similarly, protonation of the  $\sigma$ -propargyl function appears to give a  $\pi$ -allene cationic complex (171). Many of these protonation reactions reverse on addition of base.

Carbene complexes seem to form by protonation of methoxymethyl derivatives of molybdenum and iron (172–174).



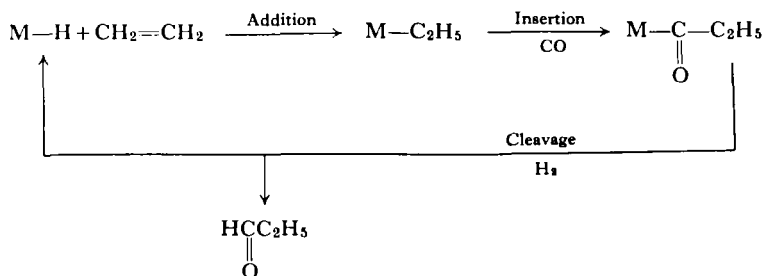
The carbene complexes were not isolable but did serve as carbene carriers for transformation of cyclohexene to norcaradiene. A similar reaction was observed when chloromethyl derivatives were treated with  $\text{AgBF}_4$ .

### D. Catalysis

Alkyl derivatives of the transition metals are key intermediates in many catalytic reactions of olefins. These intermediates are well characterized in

homogeneous catalysis but only recently has it become apparent that similar alkyl species exist on the surfaces of heterogeneous catalysts.

One general mechanism for catalysis of olefin reactions is the three-step sequence illustrated for the hydrocarbonylation of ethylene.



The addition of the metal hydride to the olefin to give an alkyl derivative is common to all the catalytic reactions discussed below. The second step involves an insertion into the C—M bond as discussed in Section IV,B. The cleavage step must give a metal hydride or, at least, some species that can be converted to a metal hydride if the process is to be truly catalytic.

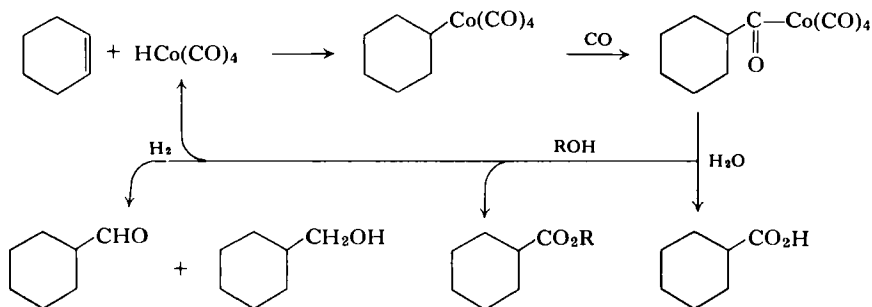
Another family of catalytic reactions of olefins, typified by the Smidt process for oxidation of ethylene to acetaldehyde, proceeds by a different mechanism. In these reactions a nucleophile such as  $\text{OH}^-$ ,  $\text{Cl}^-$ , or acetate ion attacks a coordinated olefin. A  $\sigma$ -alkylpalladium compound may form as a short-lived intermediate, as discussed in a recent review by Aguilo (175).

### 1. Carbonylation

The carbonylation of olefins to aldehydes, carboxylic acids, and esters is an important industrial process. The most common carbonylation catalyst is  $\text{Co}_2(\text{CO})_8$ , although  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ , rhodium salts, and mixtures of platinum and tin chlorides are effective catalysts. The cobalt carbonyl, whether preformed or formed *in situ* by reduction of cobalt salts, reacts with hydrogen, water, or alcohol to give  $\text{HCo}(\text{CO})_4$ , which appears to be the true catalyst (3, 176). In the catalytic cycle illustrated below with cyclohexene as the substrate, the Co—H bond adds to the olefin to give cyclohexylcobalt carbonyl. Carbon monoxide insertion gives an acyl derivative which is then cleaved to regenerate  $\text{HCo}(\text{CO})_4$  and the organic product. The nature of this product is determined by the cleavage reagent. Hydrogen



gives a mixture of aldehyde and alcohol; water and alcohols give carboxylic acid derivatives. The solvolytic cleavage of the C—M bond occurs in the opposite direction to that usually observed with alkyl derivatives of the transition metals (Section IV,A,1) but, fortunately, the acyl group polarizes the C—M bond in such a way that the “inverse” cleavage is favored (111).

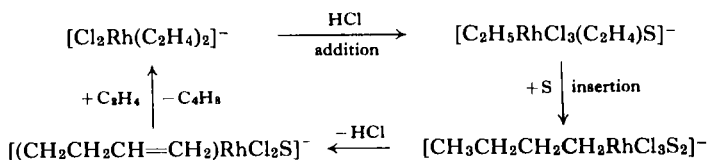


The addition of the Co—H bond to unsymmetrical olefins is relatively nonspecific. Propylene ordinarily gives mixtures of butyraldehyde and isobutyraldehyde although the former appears to predominate (176). Phosphines, which are sometimes added as carbonylation catalyst “promoters,” favor the formation of straight-chain products from terminal olefins.

The synthesis of acrylic esters from acetylene, CO, and alcohols probably involves a similar three-step mechanism with  $\text{CH}_2=\text{CH}-\text{M}$  as the initial addition product. Nickel carbonyl in aqueous acid is the preferred catalyst (176).

## 2. Olefin Dimerization and Polymerization

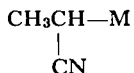
The homogeneous catalytic dimerization of olefins, e.g., ethylene to butene, is another important reaction that can proceed via the addition, insertion, cleavage sequence. Among the catalysts that effect ethylene dimerization are  $\text{RhCl}_3$ ,  $\text{PdCl}_2$ , and combinations of alkylaluminum halides with divalent iron, cobalt, and nickel compounds. The rhodium system has been thoroughly studied (177) and almost certainly proceeds by the sequence shown below ( $\text{S} = \text{solvent}$ ). The nickel system probably functions similarly, but other mechanisms have been considered for the iron-, cobalt-, and palladium-catalyzed reactions.



In this sequence, ethylene reduction of  $\text{RhCl}_3$  gives the initial rhodium(I) complex. The addition step may involve transient formation of an  $\text{Rh}-\text{H}$  bond by protonation of the rhodium or can occur by direct protonation of a coordinated ethylene. The solvent-promoted insertion resembles the base-assisted carbonyl insertion in  $\text{CH}_3\text{Mn}(\text{CO})_5$  (Section IV,B,1). Elimination of a proton from the  $\beta$ -carbon of the *n*-butyl group gives a  $\pi$ -complex of butene which is then displaced by ethylene to regenerate the original catalyst.

A similar insertion of ethylene into a  $\text{C}-\text{M}$  bond of a  $\pi$ -butenyl complex seems to occur in the industrial synthesis of hexadienes from butadiene and ethylene, at least with rhodium and nickel compounds. These catalysts give *trans*-1,4-hexadiene as the initial product (178). Cobalt and iron catalysts give the *cis* isomer (179, 180), probably by a different mechanism.

Functionally substituted olefins such as acrylonitrile also dimerize by a mechanism similar to that described for ethylene. Acrylonitrile, with  $\text{H}_2$  and a ruthenium catalyst, gives a mixture of dicyanobutenes and adiponitrile (181). The formation of linear products indicates that the addition gives  $\text{NCCH}_2\text{CH}_2-\text{Ru}$  in contrast to

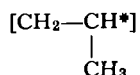


reported from addition of acrylonitrile to cobalt (182) and rhodium hydrides (183).

The success of the dimerization reaction depends on elimination of a hydrogen from the  $\beta$ -carbon of the insertion product to give the olefin dimer. If this elimination does not take place, continued insertion of olefin into the  $\text{C}-\text{M}$  bond gives a high polymer such as  $\text{H}(\text{CH}_2\text{CH}_2)_n-\text{M}$ .

Olefin polymerization by transition metal complexes such as those in the catalyst systems of Ziegler and Natta is remarkably stereospecific. A mixture of an alkylaluminum halide and  $\text{TiCl}_4$  polymerizes ethylene at low pressure to crystalline linear polyethylene (184) with a relatively high density (0.96) and melting point ( $132^\circ\text{C}$ ). These properties contrast sharply

with those ( $d$  0.92, m.p. 112°–115° C) of polyethylene prepared by conventional high-pressure, free radical polymerization which gives a polymer chain with many methyl branches. An even more dramatic effect of the Natta catalyst,  $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{AlCl}$  and  $\alpha\text{-TiCl}_3$ , is the polymerization of higher olefins in a stereoregular manner. In the polymerization of propylene, each added olefin generates an asymmetric center.

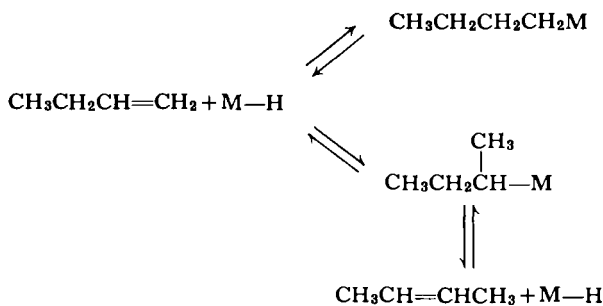


Proper choice of reaction conditions gives either *isotactic* polymer (all methyl groups on the same side of the zigzag chain) or *syndiotactic* polymer (alternating  $d$  and  $l$  sites).

The polymerization mechanism involves repeated insertion of olefin into the C—M bond of the growing alkyl chain but many details of the process remain unclear because the catalyst systems are extraordinarily difficult to study. The stereoregularity of the Natta polymers may result from stereospecific coordination of the olefin to an asymmetric site on the  $\text{TiCl}_3$  crystal adjacent to the growing polymer chain (184a).

### 3. Olefin Isomerization

Many transition metal hydrides and low-valent complexes that can generate an M—H bond by protonation catalyze hydrogen migrations in olefins. Rhodium trichloride or rhodium(I) compounds plus HCl rapidly isomerize 1-butene to an equilibrium mixture of butenes in which *trans*-2-butene is the largest single component. Most of the complexes that catalyze olefin dimerization also catalyze isomerization. The isomerization mechanism postulated by Cramer is similar to his dimerization mechanism except that no insertion step is involved (185).



As illustrated for 1-butene, the initial step in this isomerization scheme is M—H addition to the olefin double bond. If the metal adds to the terminal position to give an *n*-butyl derivative, reversal by  $\beta$ -hydrogen elimination regenerates 1-butene. However, the *sec*-butyl complex formed by addition in the opposite direction can undergo  $\beta$ -elimination to give either 1- or 2-butene. Rotation about the C—C bonds in the *sec*-butyl group permits formation of either *cis*- or *trans*-2-butene. With a rhodium catalyst, the addition-elimination cycle is rapid, as judged by the rate of H—D exchange when a hydrocarbon olefin is isomerized in a DCl—D<sub>2</sub>O medium.

An isomerization mechanism which does not involve a  $\sigma$ -alkyl intermediate has been postulated for catalysts such as Pd complexes which are prone to form  $\pi$ -allyl derivatives. Isomerization of 1-butene by this scheme would proceed by transfer of a hydrogen from the 3-carbon to the metal to give a  $\pi$ -butenyl complex. Subsequent hydrogen transfer from the metal to the 1-carbon yields 2-butene. Evidence for such a 1,3-hydrogen transfer has been reported (186).

#### 4. Olefin Hydrogenation

One common mechanism for olefin hydrogenation by either homogeneous or heterogeneous catalysts is M—H addition followed by hydrogenolysis of a C—M bond.



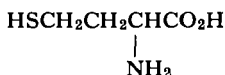
Evidence for such a scheme has been presented for hydrogenations conducted with simple Ru(II) salts, HCo(CO)<sub>4</sub>, [HCo(CN)<sub>5</sub>]<sup>3-</sup>, or [Pt(SnCl<sub>3</sub>)<sub>5</sub>]<sup>3-</sup> as catalysts (188–191). These homogeneous catalysts function best with terminal olefins and acetylenes. With dienes as substrates, the anionic catalysts selectively hydrogenate only one of the two double bonds. These complexes also catalyze olefin isomerization and, in the case of nonconjugated dienes, isomerization to a conjugated diene may precede hydrogenation.

A second hydrogenation mechanism is the simultaneous transfer of two hydrogen atoms from a dihydride complex to a coordinated olefin. Fairly strong evidence, including stereospecific *cis* addition of D<sub>2</sub> to an internal olefin, indicates that (Ph<sub>3</sub>P)<sub>3</sub>RhCl functions in this way (192). Stereospecific addition of D<sub>2</sub>, however, can also occur in the two-step process, as pointed out by Halpern in a study of catalysis by Ru(II) salts (188).

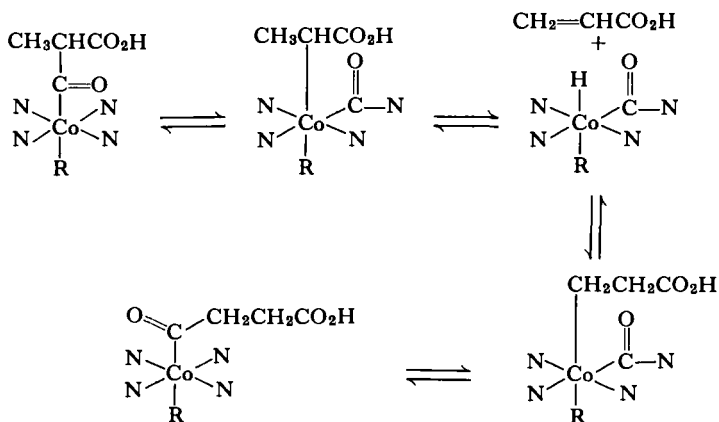
### E. Biological Processes

Transition metal-containing enzymes catalyze many important biological processes. Vitamin B<sub>12</sub>, in particular, forms C—Co bonds in its conversion to coenzymes that catalyze isomerization and transmethylation reactions. The vitamin, usually isolated as a dicyano derivative, contains a trivalent cobalt in a near-octahedral environment formed by the two cyanides and a planar, tetradentate, porphyrinlike ligand (the corrin ring). Reduction of the Co(III) complex gives first a yellow-brown Co(II) compound (B<sub>12r</sub>) and then a yellow-green species (B<sub>12s</sub>). The latter is probably a Co(I) complex although it undergoes addition reactions with olefins, fluoro-olefins, acetylenes, and diazomethane that are ordinarily considered characteristic of a metal hydride (193). Attempts to detect a Co—H bond spectroscopically have been unsuccessful.

In nature, vitamin B<sub>12s</sub> reacts with active esters such as an adenosine phosphate to give a C—Co bond. In one common coenzyme form, the ligand is adenosine which is bound through the 5-carbon of a ribose. Another coenzyme form has a methyl group bound to the cobalt. The CH<sub>3</sub> may be transferred to the sulfur atom of homocysteine



in methionine biosynthesis. Acyl derivatives are evidently involved in the isomerization of methylmalonic acid to succinic acid, a key step in propionate metabolism. Whitlock (194) has proposed the following mechanism, which embodies several familiar aspects of organometallic chemistry:





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# Organometallic Nitrosyls

W. P. GRIFFITH

*Department of Inorganic Chemistry  
Imperial College, University of London  
London, England*

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## I

### INTRODUCTION

Transition metal compounds containing nitric oxide as a coordinated ligand are normally called nitrosyl complexes. However, the term "nitrosyl", is only sometimes restricted specifically to complexes which can be regarded as containing a three-electron metal-nitric oxide bond, and the term seems to be used generally for all nitric oxide compounds. Although there are many transition metal-nitrosyl complexes, relatively few also contain metal-carbon linkages and therefore fall within the subject of this chapter.

Of the organometallic nitrosyls which have been reported, the great majority are simple substitution products of cobalt nitrosyl carbonyl,  $\text{Co}(\text{NO})(\text{CO})_3$  and of iron nitrosyl carbonyl,  $\text{Fe}(\text{NO})_2(\text{CO})_2$ . Recently, however, there has been research activity on cyclopentadienyl nitrosyls, nitrosyl pentacyanides, and alkyl and allyl nitrosyls.

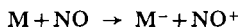
The general topic of transition metal nitrosyl chemistry has been ably treated by Johnson and McCleverty (48), and this more restricted survey owes much to that review. Here we shall briefly consider the nature of the metal-ligand link in organometallic nitrosyls, the preparative chemistry of the main classes of compounds, and the physical data which have been derived for them, laying particular stress on the more recent developments.

## II

### BONDING

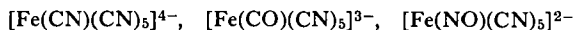
Although the nitric oxide may be capable of bonding to transition metal atoms in a number of ways (48), it appears from the physical data available that the majority of organometallic nitrosyls involve a three-electron metal-nitrosyl linkage. The precise nature of this three-electron bond remains a subject of some speculation, and recent work on the electronic and electron spin resonance spectra of nitrosyl pentacyano species makes it clear that a correct account of metal-nitrosyl bonding can only be given by a full molecular orbital approach allowing for considerable metal-ligand electron delocalization (68). However, until many more experimental data on the structures and spectra of nitrosyls become available it would appear reasonable, for descriptive purposes at least, to accept the following simple three-electron picture of metal-nitrosyl bonding.

The nitric oxide molecule has one electron in an antibonding molecular orbital; this electron is fairly easily lost (the ionization potential of NO is 9.4 eV) to give the nitrosonium ion,  $\text{NO}^+$ , which has a shorter bond length (1.062 Å) than nitric oxide (1.151 Å). We may consider the process of coordination of a nitric oxide molecule to a transition metal atom to involve the transfer of the antibonding electron from NO to the metal atom



and coordination of the nitrosonium group to M by an electron pair in an *sp* orbital of the nitrogen; thus *three* electrons are involved in the metal-nitrosyl bond. It is a consequence of this three-electron transference (or, an equivalent description, a consequence of the electron-pair coordination

of the positively charged nitrosonium group) that the *formal* oxidation state of the metal atom must decrease by one upon such coordination. Thus the nitroprusside ion  $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$  involves iron(II) rather than iron(III), the ligands involved being  $\text{NO}^+$  and  $5\text{CN}^-$ , so that the three species



are isoelectronic, all containing iron(II). It should also be noted that the three ligands  $\text{CN}^-$ , CO, and NO are isoelectronic.

Direct evidence that this type of linkage is involved in nitrosyl pentacyano complexes has been obtained from spectroscopic studies, and a molecular orbital description has been given (48, 68). Infrared measurements suggest that an N—O stretching frequency in the range  $1550\text{--}1950\text{ cm}^{-1}$  may be associated with a terminal NO group coordinated in this way; bridging nitrosyls show N—O stretches near  $1450\text{ cm}^{-1}$  or even as low as  $1320\text{ cm}^{-1}$  if the NO group bridges three metal atoms; see Section V, A).

Measurements of electronic spectra show that the nitrosyl ligand has a very substantial  $\pi$ -acceptor capacity, certainly greater than have CO or  $\text{CN}^-$ , and for this reason nitrosyl complexes very often conform to the inert gas rule, as do most carbonyls and many cyanides.

### III

#### STRUCTURAL DATA

Unfortunately few data are available, and this paucity of structural information is found throughout the field of nitrosyl chemistry. There have been only four high-accuracy X-ray measurements on organometallic species, those on  $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ , on  $\text{CpCr}(\text{NO})_2$ , on  $\text{Mn}(\text{NO})(\text{CO})_2(\text{PPh}_3)_2$ , and on  $\text{Cp}_3\text{Mn}_3(\text{NO})_4$  (see below).<sup>1</sup> In addition, there are early electron diffraction measurements on  $\text{Fe}(\text{NO})_2(\text{CO})_2$  and  $\text{Co}(\text{NO})(\text{CO})_3$  (7), and a microwave study of  $\text{CpNi}(\text{NO})$  (13), but these investigations did not yield bond parameters of high accuracy. The available results are summarized in Table I.

The structure of  $\text{CpCr}(\text{NO})_2$  is remarkable in that it demonstrated unequivocally for the first time the existence of bent M—N—O bonds in a nitrosyl complex. Although bent M—N—O bonds have been claimed in  $\text{Co}(\text{NO})(\text{S}_2\text{CNMe}_2)_2$  (1) and in a number of ruthenium complexes (48) the evidence is not conclusive. Electron spin resonance measurements on

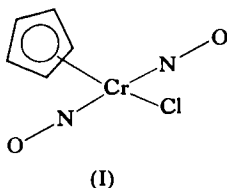
<sup>1</sup> Throughout this chapter, Cp refers to the  $\pi\text{-C}_5\text{H}_5$  group.

TABLE I  
STRUCTURAL DATA FOR ORGANOMETALLIC NITROSYLS

Complex	M—N distance (Å)	N—O distance (Å)	M—N—O angle	Other bond distances (Å)	References
CpCr(NO) <sub>2</sub>	1.704 ± 0.013 1.717 ± 0.012	1.152 ± 0.019 1.128 ± 0.018	166.4° ± 1.3° 170.8° ± 1.3°	Cr—Cl = 2.311 ± 0.005	9 <sup>a</sup>
K <sub>3</sub> [Cr(NO)(CN) <sub>5</sub> ]	—	—	—	Cr—C = 1.99 ± 0.03 C—N = 1.05 ± 0.12	95 <sup>a</sup>
K <sub>3</sub> [Mn(NO)(CN) <sub>5</sub> ]	1.66 ± 0.01	1.21 ± 0.02	174.3 ± 1.3°	Mn—C = 1.97 ± 0.02	93 <sup>a</sup>
Mn(NO)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	1.73 ± 0.01	1.18 ± 0.01	178°	Mn—P = 2.278 ± 0.005 Mn—C = 1.78 ± 0.02	17b <sup>a</sup>
Na <sub>2</sub> [Fe(NO)(CN) <sub>5</sub> ] · 2H <sub>2</sub> O	1.63 ± 0.02	1.13 ± 0.02	178.3° ± 1.3°	Fe—C = 1.90 ± 0.02 C—N = 1.16 ± 0.03	69 <sup>a</sup>
Fe(NO) <sub>2</sub> (CO) <sub>2</sub>	1.77 ± 0.02	1.12 ± 0.03	180°	Fe—C = 1.84 ± 0.02 C—O = 1.15 ± 0.03	7 <sup>b</sup>
Na <sub>2</sub> [Ru(NO)(OH)(NO <sub>2</sub> ) <sub>4</sub> ] · 2H <sub>2</sub> O	1.748 ± 0.004	1.127 ± 0.007	179.9° ± 0.55°	Ru—NO <sub>2</sub> = 2.080 ± 0.003	87 <sup>c</sup>
Co(NO)(CO) <sub>3</sub>	1.76 ± 0.03	1.10 ± 0.04	180°	Co—C = 1.83 ± 0.02	7 <sup>b</sup>
CpNi(NO)	1.67 ± 0.02	—	180°	N—O = 1.10 ± 0.03 (ass.)	13 <sup>d</sup>
Cp <sub>3</sub> Mn <sub>3</sub> (NO) <sub>4</sub>	—	—	—	Mn—Mn = 2.50	17a <sup>a</sup>

<sup>a</sup> X-ray diffraction.<sup>b</sup> Electron diffraction.<sup>c</sup> Neutron diffraction.<sup>d</sup> Microwave spectra.

$K_3[Cr(NO)(CN)_5]$  have suggested that this has bent  $M-N-O$  bonds (65), but a preliminary X-ray shows that this is not the case (95). Moreover, an X-ray of  $Fe(NO)(S_2CNEt_2)_2$  shows that this has linear  $M-N-O$  bonds (10a); this is also the situation in  $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$  (69) and in  $Na_2[Ru(NO)(OH)(NO_2)_4] \cdot 2H_2O$  (87). In the case of  $CpCr(NO)_2$ , which



has structure (I), the  $Cr-N-O$  angles are  $168^\circ \pm 1^\circ$ . It appears that this deviation from linearity is probably not due to packing effects but is rather to be associated with electrostatic repulsions between the chlorine and oxygen atoms, which are indeed quite close in the molecule; the bending occurs in a plane perpendicular to that of the  $CrN_2$  triangle (9). The microwave spectrum of  $CpNi(NO)$ , while it did not give bond lengths, did indicate that the  $Ni-N-O$  group is linear (13). In  $Mn(NO)(CO)_2(PPh_3)_2$ , which has a trigonal bipyramidal structure with axial phosphine groups, the  $Mn-N-O$  grouping is linear (17b).<sup>2</sup>

Irradiation of a solution of the complex  $[CpMn(CO)(NO)]_2$  affords a compound which was first assigned the molecular formula  $Cp_6Mn_6(NO)_8$  (58). A number of structures were proposed (48, 58) to account for the way in which the presumed  $Mn_6$  cluster was held together. Recently this problem has been resolved by a single-crystal X-ray study (17a). The molecular formula was thereby established as  $Cp_3Mn_3(NO)_4$ . The structure consists of a triangle of manganese atoms in which a nitrosyl group acts as a triply bridging ligand. A cyclopentadienyl group is bonded to each manganese atom. Along each side of the metal atom triangle is a doubly bridging nitrosyl group bent up above the plane, while the triply bridging NO is normal to and below the  $Mn_3$  plane. This structure is in accord with the infrared spectrum ( $\nu_{NO}$  at 1543, 1481, and  $1328\text{ cm}^{-1}$ ) and proton NMR ( $\tau$  4.94 singlet). In its capacity of bridging three metal atoms the NO

<sup>2</sup> Recently, the presence of a bent  $M-N-O$  linkage with an angle of  $124^\circ$  in  $\{Ir(CO)Cl(NO)[P(C_6H_5)_3]_2\}BF_4$  has been demonstrated by X-ray methods; the  $Ir-N$  and  $N-O$  distances are 1.97 and 1.16 Å, respectively [D. J. Hodgson, N. C. Payne, J. A. McGinney, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.* **90**, 4486 (1968)].



group can be added to a number of other ligands with this ability, e.g., CO in  $\text{Rh}_6(\text{CO})_{16}$ ,  $[\text{CpFeCO}]_4$ , or  $\text{Fe}_4(\text{CO})_{13}^{2-}$ ; and even H in  $\text{HRh}_3\text{Cp}_4$ .

The metal–nitrogen bond distances in  $\text{CpCr}(\text{NO})_2$ ,  $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ , and  $\text{Na}_2[\text{Ru}(\text{NO})(\text{OH})(\text{NO}_2)_4] \cdot 2\text{H}_2\text{O}$  are all significantly shorter than the expected distance for a metal–nitrogen single bond. This point is well exemplified by the ruthenium complex, in which the ruthenium–nitrogen (nitrosyl) distance is  $1.748 \pm 0.004 \text{ \AA}$  and the ruthenium–nitrogen (nitro) distance is  $2.080 \pm 0.003 \text{ \AA}$  (87). This is consistent with the proposition that the nitrosonium group is a very efficient  $\pi$ -acceptor, due in part to its high effective electronegativity.

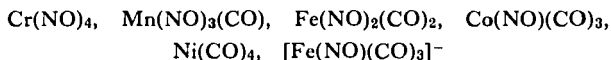
## IV

### PREPARATIONS AND CHEMICAL PROPERTIES

Before reviewing the other physical data on organometallic nitrosyls we now summarize the purely chemical information on the compounds. For convenience the material has been divided into three main categories: (a) nitrosyl carbonyls and nitrosyl isocyanides; (b) nitrosyl cyano species; and (c) cyclopentadienyl and miscellaneous organometallic nitrosyls.

#### A. Nitrosyl Carbonyls

The known examples are summarized in Table II. The simplest species are  $\text{Mn}(\text{NO})_3(\text{CO})$ ,  $\text{Fe}(\text{NO})_2(\text{CO})_2$ , and  $\text{Co}(\text{NO})(\text{CO})_3$ , all members of an isoelectronic series which can be regarded as based on nickel carbonyl.

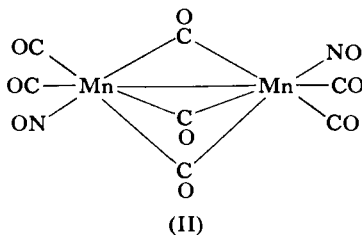


The complex  $\text{Cr}(\text{NO})_4$  is as yet unknown. Similarly,  $\text{V}(\text{NO})(\text{CO})_5$  is isoelectronic with  $\text{Cr}(\text{CO})_6$ ,  $\text{Mn}(\text{NO})(\text{CO})_4$  with  $\text{Fe}(\text{CO})_5$ , and  $\text{Mn}_2(\text{NO})_2(\text{CO})_7$  with  $\text{Fe}_2(\text{CO})_9$ . All nitrosyl carbonyls and their substitution products conform to the inert gas formalism, in which for the purposes of electron accounting the nitric oxide molecule is assumed to donate three electrons and the carbonyl group two, to the metal atom.

The vanadium and manganese complexes are the least stable and least studied of the series. The compound  $\text{V}(\text{NO})(\text{CO})_5$ , a violet solid, is made by the action of nitric oxide on vanadium carbonyl (42), while  $\text{Mn}(\text{NO})(\text{CO})_4$ , a red liquid freezing at  $-1.5^\circ \text{C}$ , is best made by treating  $\text{Mn}_2(\text{CO})_8 \cdot (\text{PPh}_3)_2$  with nitric oxide. The mechanism of this reaction has been briefly

discussed (96). The green crystalline trinitrosyl  $\text{Mn}(\text{NO})_3(\text{CO})$  is made by the action of nitric oxide on a solution of  $\text{Mn}(\text{NO})(\text{CO})_4$  in boiling xylene (96). The dimer  $\text{Mn}_2(\text{NO})_2(\text{CO})_7$  is obtained as a purple solid by ultraviolet irradiation of  $\text{Mn}(\text{NO})(\text{CO})_4$  (92). The best method for preparation of  $\text{Fe}(\text{NO})_2(\text{CO})_2$  is by the action of nitrite ion and acetic acid on salts containing the ion  $[\text{Fe}(\text{NO})(\text{CO})_3]^-$  (54), the latter being obtained from iron pentacarbonyl and nitrite (53). Iron dinitrosyl dicarbonyl is a red liquid, freezing at  $18.4^\circ\text{C}$  and boiling at  $110^\circ\text{C}$ . Cobalt nitrosyl tricarbonyl,  $\text{Co}(\text{NO})(\text{CO})_3$ , is also a red liquid, freezing at  $-11^\circ\text{C}$  and boiling at  $78.6^\circ\text{C}$ . It is best made by the action of nitrite and acetic acid on salts of the anion  $[\text{Co}(\text{CO})_4]^-$  (55).

Analysis of the infrared spectra of  $\text{Mn}(\text{NO})_3(\text{CO})$  (3), salts of  $[\text{Fe}(\text{NO})(\text{CO})_3]^-$  (53),  $\text{Fe}(\text{NO})_2(\text{CO})_2$  (3), and  $\text{Co}(\text{NO})(\text{CO})_3$  (64) suggests that these isoelectronic species have tetrahedral or distorted tetrahedral structures, as expected. On the basis of its infrared spectrum, it is thought that  $\text{Mn}(\text{NO})(\text{CO})_4$  has a trigonal bipyramidal configuration with the nitrosyl group in one of the axial positions ( $C_{3v}$  symmetry), and the infrared spectrum of  $\text{Mn}_2(\text{NO})_2(\text{CO})_7$  suggests that this has a structure (II) analogous to that of diiron enneacarbonyl, with which it is isoelectronic (92).



Replacement of one or two of the carbonyl groups in  $\text{Fe}(\text{NO})_2(\text{CO})_2$ , or  $\text{Co}(\text{NO})(\text{CO})_3$ , by a wide variety of ligands may easily be accomplished by direct reaction of the two reactants in an inert solvent (Table II). The relative inertness of nitrosyl groups to substitution is noteworthy. The reaction of  $\text{Fe}(\text{NO})_2(\text{CO})_2$  with diphosphines such as  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$  (70) or  $\text{P}_2\text{Me}_4$  (94a) yields  $[\text{Fe}(\text{NO})_2(\text{CO})]_2$  diphosphine, the diphosphine functioning as a bridge ligand. A mixed species  $\text{Fe}(\text{NO})_2(\text{CO})[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]\text{Co}(\text{NO})(\text{CO})_2$  has also been made (70). Reactions of iron or cobalt nitrosyl carbonyls with base have been studied (34, 35). With the cobalt complex the reaction

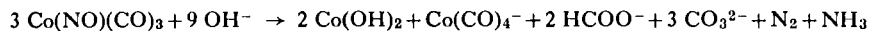


TABLE II  
NITROSYL CARBONYL AND NITROSYL ISOCYANIDE COMPLEXES\*†

Complex	Color	M.p. (°C)	$\nu_{\text{NO}}$ ( $\nu_{\text{CO}}$ )	Physical data	Preparation
V(NO)(CO) <sub>5</sub>	Violet	—	1700 (2108, 2064, 1994) <sup>a</sup>	IR (42)	(42)
V(NO)(CO) <sub>4</sub> (PPh <sub>3</sub> )	Violet	88°	1823, 1734 (2008) <sup>b</sup>	IR (98)	(98)
V <sub>2</sub> (NO) <sub>2</sub> (CO) <sub>8</sub> (Ph <sub>2</sub> P, PPh <sub>2</sub> )	Orange	—	—		(39)
Mn(NO)(CO) <sub>4</sub>	Red	−1.5°	1759 (2095, 2019, 1972) <sup>c</sup>	IR (92) KIN (96)	(52, 96)
Mn(NO) <sub>3</sub> (CO)	Green	27°	1823, 1734 (2088) <sup>a</sup>	IR (3) KIN (96)	(96)
Mn <sub>2</sub> (NO) <sub>2</sub> (CO) <sub>7</sub>	Purple	—	1743, 1734, 1731, 1726 (2102, 2042, 2006, 1995, 1976) <sup>c</sup>	IR (96)	(92)
Mn(NO)(CO) <sub>2</sub> [P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ] <sub>2</sub>	Orange	—	1635 (1925, 1834) <sup>d</sup>	IR (6) D (44) F (6)	(44)
Mn(NO)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Orange	200°	1661 (1948, 1864) <sup>d</sup>	IR (6) D (44) F (6)	(44)
Mn(NO)(CO) <sub>3</sub> (PPh <sub>3</sub> )	Red	—	1713 (2034, 1971, 1926) <sup>d</sup>	IR (6) D (44) F (6)	(44, 61)
Mn(NO)(CO) <sub>3</sub> [P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ]	Red	140°	1697 (2029, 1959, 1910) <sup>d</sup>	IR (6) D (44) F (6)	(44)
[Fe(NO)(CO) <sub>3</sub> ] <sub>2</sub> Hg	Red	110°	1785, 1770 (2071–1988) <sup>a</sup>	IR (6b)	(53)
Fe(NO) <sub>2</sub> (CO) <sub>2</sub>	Red	18° (b.p. 110°)	1810, 1756 (2087, 2034) <sup>a</sup>	IR (3) D (97) ED (7) M (23a)	(54)
Fe(NO)(CO)(CF <sub>3</sub> CO)(PPh <sub>3</sub> ) <sub>2</sub>	—	—	1710 (1931) <sup>b</sup>	IR (37)	(37)
Fe(NO)(CO)(C <sub>2</sub> F <sub>5</sub> CO)(PPh <sub>3</sub> ) <sub>2</sub>	—	—	1711 (1933) <sup>b</sup>	IR (37)	(37)
[Fe(NO)(CO) <sub>2</sub> (PPh <sub>3</sub> )] <sub>2</sub> Hg	—	—	1712, 1705 (1950, 1905) <sup>b</sup>	IR (49)	(49)
Fe(NO)(CO) <sub>2</sub> ( $\pi$ -CH <sub>2</sub> .CH.CH <sub>2</sub> )	Red	—	1761 (2038, 1938)	IR (72) NMR (72)	(8, 72)
Fe(NO)(CO) <sub>2</sub> [Fe(NO)(CO)( $\pi$ -CH <sub>3</sub> CHCH <sub>2</sub> )]	Red	—	1754 (2033, 1978)	IR (72) NMR (72)	(8, 72)
Fe(NO)(CO) <sub>2</sub> (CH <sub>3</sub> COCH.CH.CH <sub>2</sub> )	Red	—	1770 (2048, 1998)	IR (72) NMR (72)	(8, 72)
Fe(NO)(CO)( $\pi$ -RCH.CH.CH <sub>2</sub> )(PPh <sub>3</sub> ) (R = H, CH <sub>3</sub> )	Red	—	—	—	(8)
Fe(NO)(CO)(RCH=CHCH <sub>2</sub> CO)(PPh <sub>3</sub> ) (R = H, CH <sub>3</sub> )	—	—	—	—	(8)

[Fe(NO)(CO) <sub>2</sub> (Tdp) <sub>2</sub> ][Fe(NO)(CO) <sub>3</sub> ]	—	—	1755, 1634 (2025, 1963, 1860) <sup>e</sup>	IR (49) NMR (49)	(49)
Fe(NO) <sub>2</sub> (CO)(PPh <sub>3</sub> )	Red	138°	1766, 1721 (2010) <sup>a</sup>	IR (6) F (6)	(63)
Fe(NO) <sub>2</sub> (CO)[P(OEt) <sub>3</sub> ]	Red	—	—	M (23a)	(23a)
Fe(NO) <sub>2</sub> (CO)[P(OPh) <sub>3</sub> ]	Red	—	1786, 1739 (2029) <sup>a</sup>	IR (6) F (6)	(6)
Fe(NO) <sub>2</sub> (CO)[P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ]	Red	—	1753, 1711 (1997) <sup>a</sup>	IR (6) F (6)	(6)
Fe(NO) <sub>2</sub> (CO)(AsPh <sub>3</sub> )	Red	100°	1769, 1726 (2012) <sup>a</sup>	IR (6) F (6)	(63, 66)
Fe(NO) <sub>2</sub> (CO)[As( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Me) <sub>3</sub> ]	Red	130°	—	—	(66)
Fe(NO) <sub>2</sub> (CO)(SbPh <sub>3</sub> )	Orange	105°	1772, 1730 (2011) <sup>a</sup>	IR (6) F (6)	(66)
Fe(NO) <sub>2</sub> (CO)[Sb( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Me) <sub>3</sub> ]	Red	110°	—	—	(66)
Fe(NO) <sub>2</sub> (CO)(TePh <sub>2</sub> )	Red	—	1764, 1727 (2012) <sup>e</sup>	IR (38)	(38)
Fe(NO) <sub>2</sub> (CO)(diphos)Co(NO)(CO) <sub>2</sub>	Red	144°	1761, 1716 (2040, 2013, 1979) <sup>f</sup>	IR (70)	(70)
[Fe(NO) <sub>2</sub> (CO)(CN)] <sup>-</sup>	Red	—	—	—	(26)
Fe <sub>2</sub> (NO) <sub>4</sub> (CO) <sub>2</sub> (P <sub>2</sub> Me <sub>4</sub> )	Orange	70°	1764, 1730 (2012, 1987) <sup>e</sup>	IR (33) NMR (33)	(33)
Fe <sub>2</sub> (NO) <sub>4</sub> (CO) <sub>2</sub> [Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ]	Red	140°	1760, 1713 (2013) <sup>f</sup>	IR (70) KIN (70)	(70)
Fe(NO) <sub>2</sub> (CH <sub>3</sub> NC) <sub>2</sub>	Red	150°	—	—	(43)
Fe(NO) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> NC) <sub>2</sub>	Red	97°	—	—	(43)
Fe(NO) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> NC) <sub>2</sub>	Red	140°	—	—	(43, 67)
Fe(NO) <sub>2</sub> ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NC) <sub>2</sub>	Red	197°	—	—	(67)
Fe(NO) <sub>2</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NC) <sub>2</sub>	Red	180°	—	D (67)	(67)
Fe(NO) <sub>2</sub> ( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> NC) <sub>2</sub>	Orange	197°	—	D (67)	(67)
Co(NO)(CO) <sub>3</sub>	Red	-11° (b.p. 78.5°)	1822 (2108, 2047)	IR (6c, 64) D (97) F (64) ED (7) M (23a) KIN (90, 91)	(55)
Co(NO)(CO)(PPh <sub>3</sub> ) <sub>2</sub>	Red	177°	1714 (1957) <sup>a</sup>	IR (94a) F (94a)	(36, 66)
Co(NO)(CO)[P(OPh) <sub>3</sub> ] <sub>2</sub>	Yellow	84°	1765 (2004) <sup>a</sup>	IR (94a) F (94a)	(36, 66)
Co(NO)(CO)[P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ] <sub>2</sub>	Red	135°	1690 (1927) <sup>a</sup>	IR (94a) F (94a)	(36)
Co(NO)(CO)[PPh <sub>2</sub> (Et <sub>2</sub> NC <sub>2</sub> H <sub>3</sub> )] <sub>2</sub>	—	—	1715 (1948) <sup>a</sup>	IR (86)	(86)
Co(NO)(CO)[PPh <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> CN)] <sub>2</sub>	—	—	1707 (1952) <sup>g</sup>	IR (86)	(86)
Co(NO)(CO)(Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )	Red	—	1725 (1952) <sup>g</sup>	IR (34, 35)	(35)
Co(NO)(CO)[Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ]	Red	—	1705 (1959) <sup>g</sup>	IR (34, 35)	(34, 35, 70)
Co(NO)(CO)[Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub> ]	Red	—	1701 (1947) <sup>g</sup>	IR (34, 35)	(34, 35)
Co(NO)(CO)(PCl <sub>3</sub> ) <sub>2</sub>	—	—	1793 (2044) <sup>a</sup>	IR (47)	(47)

TABLE II—continued

Complex	Color	M.p. (°C)	$\nu_{\text{NO}}$ ( $\nu_{\text{CO}}$ )	Physical data	Preparation
Co(NO)(CO)(PCl <sub>2</sub> Ph) <sub>2</sub>	—	—	1772 (2024) <sup>a</sup>	IR (47)	(47)
Co(NO)(CO)(PClPh <sub>2</sub> ) <sub>2</sub>	—	—	1747 (1987) <sup>a</sup>	IR (47)	(47)
Co(NO)(CO)[PPh <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> ]	—	—	1697 (1942) <sup>g</sup>	IR (34, 35) F (34, 35)	(34, 35)
Co(NO)(CO)(PF <sub>3</sub> ) <sub>2</sub>	—	—	1822 (2059) <sup>a</sup>	IR (10) EL (10)	(10)
Co(NO)(CO)(PPh <sub>3</sub> )(AsPh <sub>3</sub> )	Red	157°	1717 (1958) <sup>d</sup>	IR (36)	(36)
[Co(NO)(CO)(CN)PPh <sub>3</sub> ](Ni phen <sub>3</sub> )	—	—	1681 (1962) (2106)†	IR (36)	(36)
Co(NO)(CO)(AsPh <sub>3</sub> ) <sub>2</sub>	Brown	126° dec	1722 (1958) <sup>d</sup>	IR (6) F (6)	(36)
Co(NO)(CO)(SbPh <sub>3</sub> ) <sub>2</sub>	Brown	119° dec	1719 (1962, 1950) <sup>b</sup>	IR (36)	(36)
Co(NO)(CO)py <sub>2</sub> §	Red	—	1745 (1967) <sup>b</sup>	IR (36)	(36)
Co(NO)(CO)bipy	Brown	—	1658 (1911) <sup>b</sup>	IR (36)	(36)
Co(NO)(CO)phen	Brown	—	1663 (1914) <sup>b</sup>	IR (36)	(36)
Co(NO)(CO)(CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NC) <sub>2</sub>	—	—	1746 (1987) <sup>a</sup>	IR (47)	(47)
Co(NO)(CO)(Me <sub>3</sub> CNC) <sub>2</sub>	—	—	1733 (1975) <sup>a</sup>	IR (47)	(47)
Co(NO)(CO) <sub>2</sub> (PPh <sub>3</sub> )	Red	130°	1760 (2036, 1982) <sup>d</sup>	IR (6) F (6)	(36)
Co(NO)(CO) <sub>2</sub> [P(OPh) <sub>3</sub> ]	Orange	60°	1781 (2053, 2001) <sup>d</sup>	IR (6) F (6)	(36)
Co(NO)(CO) <sub>2</sub> [P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ]	Red	121°	1747 (2024, 1966) <sup>d</sup>	IR (6) F (6)	(36)
Co(NO)(CO) <sub>2</sub> [P(NCH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	—	—	1764 (2052, 1995) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO) <sub>2</sub> [PPh( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> ]	—	—	1756 (2032, 1975) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO) <sub>2</sub> (PPh <sub>2</sub> Et)	—	—	1752 (2038, 1981) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO) <sub>2</sub> [P( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ]	—	—	1748 (2038, 1977) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO)[P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>3</sub> ]	—	—	1773 (2061, 2004) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO)[P(OCH <sub>3</sub> ) <sub>3</sub> ]	—	—	1764 (2050, 1996) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO) <sub>2</sub> (PEt <sub>3</sub> )	—	—	1747 (2027, 1965) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO) <sub>2</sub> [PPh <sub>2</sub> (Et <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> )]	—	—	1758 (2033, 1973) <sup>a</sup>	IR (86)	(86)
Co(NO)(CO) <sub>2</sub> [PPh <sub>2</sub> (CNC <sub>2</sub> H <sub>4</sub> )]	—	—	1762 (2040, 1984) <sup>a</sup>	IR (86)	(86)

Co(NO)(CO) <sub>2</sub> [Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sup>§</sup>	—	—	—	—	(70)
Co(NO)(CO) <sub>2</sub> (PCl <sub>3</sub> )	—	—	1806 (2073, 2030) <sup>a</sup>	IR (47) M (23a)	(47)
Co(NO)(CO) <sub>2</sub> (PCl <sub>2</sub> Ph)	—	—	1786 (2061, 2014) <sup>a</sup>	IR (47)	(47)
Co(NO)(CO) <sub>2</sub> (PClPh <sub>2</sub> )	—	—	1773 (2048, 1996) <sup>a</sup>	IR (47)	(47)
Co(NO)(CO) <sub>2</sub> (PF <sub>3</sub> )	—	—	1817 (2083, 2037) <sup>a</sup>	IR (10)	(10)
Co(NO)(CO) <sub>2</sub> (AsPh <sub>3</sub> )	Red	111°	1765 (2039, 1983) <sup>d</sup>	IR (9) F (9)	(36, 90)
Co(NO)(CO) <sub>2</sub> [As( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> ]	—	—	1753 (2035, 1975) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO) <sub>2</sub> [As( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Me) <sub>3</sub> ]	Orange	125° dec	1754 (2049, 1988) <sup>d</sup>	IR (62)	(66)
Co(NO)(CO) <sub>2</sub> [As( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ]	Red	135°	—	—	(66)
Co(NO)(CO) <sub>2</sub> (SbPh <sub>3</sub> )	Red	100°	—	—	(66)
Co(NO)(CO) <sub>2</sub> [Sb( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ]	Red	134°	—	—	(66)
Co(NO)(CO) <sub>2</sub> [Sb( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> ]	Red	150°	—	—	(66)
Co(NO)(CO) <sub>2</sub> py	—	—	1733 (2041, 1969) <sup>h</sup>	IR (90) KIN (90)	(90)
Co(NO)(CO) <sub>2</sub> [Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ]Fe(NO) <sub>2</sub> (CO)	Red	144°	1761, 1716 (2040, 2013, 1979) <sup>f</sup>	IR (70)	(70)
Co <sub>2</sub> (NO) <sub>2</sub> (CO) <sub>4</sub> (Ph <sub>2</sub> PPPh <sub>2</sub> ) <sup>§</sup>	Red	—	—	—	(39)
Co <sub>2</sub> (NO) <sub>2</sub> (CO) <sub>2</sub> (Ph <sub>2</sub> PPPh <sub>2</sub> )	Brown	—	—	—	(39)
Co <sub>2</sub> (NO) <sub>2</sub> (CO) <sub>4</sub> [Ph <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> N(Et)C <sub>2</sub> H <sub>4</sub> PPh <sub>2</sub> ]	—	—	1758 (2033, 1976) <sup>a</sup>	IR (86)	(86)
Co <sub>2</sub> (NO) <sub>2</sub> (CO) <sub>4</sub> [Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ]	—	—	1759 (2037, 1979) <sup>j</sup>	IR (70)	(70)
Co(NO)( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NC) <sub>3</sub>	Red	157°	—	D (67)	(67)
Co(NO)( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NC) <sub>3</sub>	Orange	107°	—	D (67)	(67)
Co(NO)(CO)( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NC) <sub>2</sub>	Orange	156°	—	—	(67)
Ir(NO)(CO)(PPh <sub>3</sub> ) <sub>2</sub>	Red	168°	1645 (1940) <sup>e</sup>	IR (2) D (2)	(2)

\* List of abbreviations for physical data used in Tables II–IV: D, dipole moment; ED, electron diffraction; EL, electronic spectra; ESR, electron spin resonance; F, force constant treatment; IR, infrared spectra; KIN, kinetic data; M, mass spectra; MAG, magnetic susceptibility; NMR, nuclear magnetic resonance; POL, polarography; X, X-ray diffraction.

† Media used for recording infrared spectra reported in Tables II–IV: <sup>a</sup> cyclohexane; <sup>b</sup> potassium bromide (pressed disc); <sup>c</sup> tetrachloroethylene; <sup>d</sup> carbon tetrachloride; <sup>e</sup> Nujol (mull); <sup>f</sup> dichloromethane; <sup>g</sup> chloroform; <sup>h</sup> toluene; <sup>i</sup> benzene; <sup>j</sup> as liquid film.

‡ CN.

§ Not isolated.

occurs, while with the iron complex an even more complicated process occurs, yielding  $[\text{Fe}(\text{NO})(\text{CO})_3]^-$ . The mercury salt of this an ion,  $\text{Hg}[\text{Fe}(\text{NO})(\text{CO})_3]_2$ , undergoes a number of reactions similar to those of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  (49).

### B. Nitrosyl Isocyanides

A number of such complexes have been prepared (Table II), the usual method of preparation being the action of organic isocyanides on iron or cobalt nitrosyl carbonyls, or on other nitrosyl complexes. The dipole moments of a number of the products have been measured (Table VI).

### C. Nitrosyl Cyanide Complexes

The nitrosyl cyanide complexes are listed in Table III. Although these are strictly organometallic species since they contain metal-carbon  $\sigma$ -bonds they are seldom considered as such by organometallic chemists. The information given here derives principally from the most recent references; earlier and more detailed references are given in Johnson and McCleverty's review (48). The chief method of preparation is to treat hexacyano complexes of the metals with hydroxylamine hydrochloride in basic solution, a method which can be made to give  $\text{K}_5[\text{V}(\text{NO})(\text{CN})_5]$  (29),  $\text{K}_4[\text{Mo}(\text{NO})(\text{CN})_5]$  (84),  $\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_5]$  (30),  $\text{K}_3[\text{Mn}(\text{NO})(\text{CN})_5]$  (12), and  $\text{K}_2[\text{Ni}(\text{NO})(\text{CN})_3]$  (73). The paramagnetic complexes  $\text{K}_2[\text{Mn}(\text{NO})(\text{CN})_5]$  (12) and  $\text{K}_2[\text{Cr}(\text{NO})(\text{CN})_5]$  (26) can be obtained from the lower oxidation state nitrosyl pentacyano complexes and nitric acid, while the action of nitric acid on cyano complexes of rhenium, iron, and ruthenium may be made to yield  $\text{Ag}_3[\text{Re}(\text{NO})(\text{CN})_7]$  (11),  $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$  (99), and  $\text{K}_2[\text{Ru}(\text{NO})(\text{CN})_5]$ . [A better preparation for the latter complex, involving the action of nitric oxide, has recently been described (17).] Electrolytic reduction of  $[\text{Cr}(\text{NO})(\text{CN})_5]^{3-}$  affords  $[\text{Cr}(\text{NO})(\text{CN})_5]^{4-}$  (27) and of  $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$  gives  $[\text{Fe}(\text{NO})(\text{CN})_5]^{3-}$  (45). There is a recent review on the chemistry of  $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$  (89a).

There is evidence for the existence of salts containing the ion  $[\text{Fe}(\text{NO})(\text{CN})_5]^{4-}$  (60, 94) which may, however, contain hyponitro groups (48). The salt  $\text{K}_3[\text{Co}(\text{NO})(\text{CN})_5]$  may contain a coordinated  $\text{NO}^-$  ligand (32) or a coordinated hyponitrite group (83), though the infrared evidence tends to support the former proposal.

TABLE III  
NITROSYL CYANIDE COMPLEXES\*

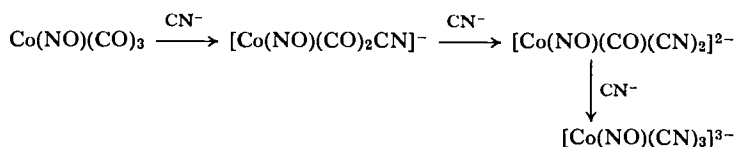
Complex	Color	$\nu_{\text{NO}}$ ( $\nu_{\text{CN}}$ )	Physical data	Preparation
$\text{K}_5[\text{V}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$	Orange	1575 (2095) <sup>e</sup>	IR (29) EL (68)	(29)
$\text{K}_4[\text{Cr}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$	Blue	1515 (2020) <sup>e</sup>	IR (27) POL (28)	(27)
$\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$	Green	1630 (2120, 2073) <sup>e</sup>	IR (25) MAG (30) EL (68) X (95) ESR (45)	(30)
$\text{K}_4[\text{Mo}(\text{NO})(\text{CN})_5]$	Purple	1455 (2108, 2080, 2060, 2040, 2023) <sup>e</sup>	IR (84)	(84)
$\text{K}_4[\text{Mo}(\text{NO})\text{O}_2(\text{CN})_5]$	Yellow	1580 (2167, 2125, 2040) <sup>e</sup>	IR (27)	(27)
$\text{K}_3[\text{Mn}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$	Purple	1700 (2130, 2101, 2060) <sup>e</sup>	IR (25) X (93) EL (68)	(12)
$\text{Zn}[\text{Mn}(\text{NO})(\text{CN})_5]$	Yellow	1885 (2195, 2150) <sup>e</sup>	IR (68) MAG (12) EL (68) ESR (68)	(12)
$\text{Ag}_3[\text{Re}(\text{NO})(\text{CN})_7]$	Purple	1875 <sup>e</sup>	IR (11)	(11)
$\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$	Red	1935 (2170–2098) <sup>e</sup>	IR (86a) EL (68) X (69) POL (60) KIN (89a)	(99)
$[\text{Fe}(\text{NO})(\text{CN})_5]^{3-}\dagger$	Brown/blue	—	MAG (28) ESR (45) EL (45)	(45)
$\text{K}_2[\text{Ru}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$	Red	1915 <sup>e</sup>	IR (17)	(17)
$\text{K}_2[\text{Co}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$	—	—	X (76)	—
$\text{K}_3[\text{Co}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$	Yellow	1150 (2141, 2104) <sup>e</sup>	IR (32)	(75)
$\text{K}_2[\text{Co}(\text{NO})(\text{CO})_2(\text{CN})]$	Red	1720 (2102, 2037, 1960) <sup>e</sup>	IR (31)	(75)
$\text{K}_2[\text{Co}(\text{NO})(\text{CO})(\text{CN})_2]$	Red	—		(75)
$\text{K}_2[\text{Co}(\text{NO})(\text{CN})_3]$	Red	—		(75)
$\text{K}_2[\text{Ni}(\text{NO})(\text{CN})_3]$	Purple	1780 (2133, 2118) <sup>e</sup>	IR (26)	(73)

\* See footnotes to Table II.

† Not isolated.



A few *nitrosyl carbonyl cyanides* are known. Reaction of  $\text{Co(NO)(CO)}_3$  with potassium cyanide successively removes the carbonyl groups (36).



Other ions of this type are  $[\text{Fe(NO)}_2(\text{CO})(\text{CN})]^-$  (70), and  $[\text{Co(NO)(CO)-}(\text{CN})(\text{PPh}_3)]^-$  (36).

### D. Cyclopentadienyl Nitrosyls

Complexes of this type are summarized in Table IV.

#### 1. Complexes with Terminal Nitrosyl Groups

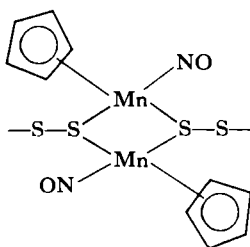
Although a fairly large number of these are now known they can be classified in two isoelectronic series:

- (i)  $[\text{CpMn(NO)(CO)}]_2$ ,  $[\text{CpMn(NO)}_2]_2$ ,  $[\text{CpCr(NO)}_2]_2$ ,  $[\text{CpFe(CO)}_2]_2$
- (ii)  $[\text{CpCr(NO)}_2\text{CO}]^+$ ,  $\text{CpCr(NO)}_2\text{X}$ ,  $[\text{CpMn(NO)(CO)}_2]^+$ ,  $\text{CpMn(NO)(CO)X}$ ,  $\text{CpFe(CO)}_2\text{X}$

The chromium complex  $\text{CpCr(NO)}_2\text{Cl}$  can most easily be prepared from chromic chloride, sodium cyclopentadienide, and nitric oxide (50); the structure of the complex is discussed in Section III. From this, or the corresponding bromide, a number of complexes of the type  $\text{CpCr(NO)}_2\text{X}$  can be made by metathetical reactions (78, 79).

The nitrosyl carbonyls  $\text{CpM(NO)(CO)}_2$  [ $\text{M} = \text{Cr}$  (21, 78),  $\text{Mo}$  (57),  $\text{W}$  (19)] can be made by the action of nitric oxide on  $[\text{CpCr(CO)}_3]_2$ ,  $[\text{CpMo(CO)}_3]^-$ , or  $[\text{CpW(CO)}_3]^-$ , respectively. The chromium complex undergoes a Friedel-Crafts acetylation to give  $(\text{C}_5\text{H}_4\text{COCH}_3)\text{Cr(NO)(CO)}_2$  (21). A series of molybdenum complexes  $\text{CpMo(NO)I}_2\text{L}$  [ $\text{L} = \text{PPh}_3$ ,  $\text{P(OPh)}_3$ ,  $\text{py}$ , and  $\text{bipy}$ ] has been made from  $\text{L}$  and  $[\text{CpMo(NO)I}_2]_2$  (57). The cationic manganese species  $[\text{CpMn(NO)(CO)}_2]^+$ , obtained by the action of nitrite and acid on  $\text{CpMn(CO)}_3$ , can be precipitated as the yellow hexafluorophosphate salt (51). With sodium borohydride this affords  $[\text{CpMn(NO)(CO)}]_2$  which probably contains bridging  $\text{NO}$  groups (see below) (58). The complex  $[\text{CpMn(NO)S}_2]_n$  is probably similar in structure

(III) to the Roussin red salts, containing bridging sulfide groups. It is made by the action of carbon disulfide on  $\text{Cp}_3\text{Mn}_2(\text{NO})_3$  (80).



(III)

A strong band at  $491\text{ cm}^{-1}$  in the infrared spectrum probably arises from an S—S stretch (80). The acetate and acetyl derivatives  $\text{CpMn}(\text{NO})(\text{CO})\text{-(MeCOO)}$  and  $\text{CpMn}(\text{NO})(\text{CO})(\text{MeCO})$  have been reported; the former was obtained by the action of sodium methoxide on  $[\text{CpMn}(\text{NO})(\text{CO})_2]^+$ , and the acetyl complex is made from the acetate and methylmagnesium bromide (59).

The Group VIII cyclopentadienyl complexes of formula  $\text{CpM}(\text{NO})$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ) have all been synthesized. The nickel complex is best prepared from nickelocene and nitric oxide, and a method for the preparation of the nickelocene *in situ* without its isolation has been described (56). The palladium complex can be prepared from  $[\text{Pd}(\text{NO})\text{Cl}]_n$  and sodium cyclopentadienide (23); and the platinum complex from  $\text{Pt}_2(\text{CO})_2\text{Cl}_4$  and sodium cyclopentadienide and nitric oxide (22). The microwave (13) and infrared spectra (18) of  $\text{CpNi}(\text{NO})$  have received detailed study, and the electronic structure of the complex is discussed in an early paper (77).

## 2. Complexes with Bridging Nitrosyl Groups

In all the complexes so far described it is fairly certain that the nitrosyl group is monodentate. There are, however, a few species, notably of manganese, and all containing the cyclopentadienyl group, which appear to involve bridging nitrosyl groups.

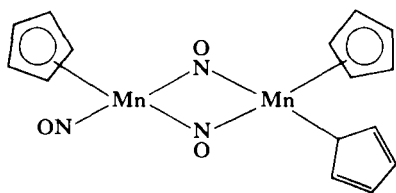
The first of these to be prepared was  $\text{Cp}_3\text{Mn}_2(\text{NO})_3$ , obtained from bis(cyclopentadienyl)manganese and nitric oxide (58, 78). The proton magnetic resonance spectrum of this compound shows two broad bands ( $\tau \sim 4.7$  and  $5.6$ , of relative intensities 2:1), suggesting the presence of two different types of cyclopentadienyl ring. It has been proposed that structures (IV) or (V) are reasonable for the compound (58, 78):

TABLE IV  
CYCLOPENTADIENYL AND MISCELLANEOUS ORGANOMETALLIC NITROSYLS\*

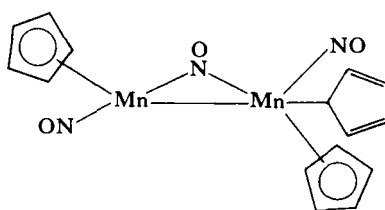
Complex	Color	M.p. (°C)	$\nu_{\text{NO}}$ ( $\nu_{\text{CO}}$ )	Physical data	Preparation
CpCr(NO)(CO) <sub>2</sub>	Orange	67°	1712 (2028, 1961)	IR (21) D (97)	(21, 78)
( $\pi$ -C <sub>5</sub> H <sub>4</sub> COCH <sub>3</sub> )Cr(NO)(CO) <sub>2</sub>	Red	27°	1812 (2032, 1961)	IR (21)	(21)
CpCr(NO) <sub>2</sub> Cl	Green	140° dec	1818, 1711 <sup>g</sup>	IR (78) X (9)	(50, 78)
CpCr(NO) <sub>2</sub> Br	Green	—	1820, 1717 <sup>g</sup>	IR (79)	(79)
CpCr(NO) <sub>2</sub> I	Black	143°	1810, 1685 <sup>e</sup>	IR (58) (NMR (58)	(58)
CpCr(NO) <sub>2</sub> (NCS)	Green	165° dec	1827, 1723 <sup>g</sup>	IR (78)	(78)
CpCr(NO) <sub>2</sub> CH <sub>3</sub>	Green	83°	1779, 1670 <sup>d</sup>	IR (79)	(79)
CpCr(NO) <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	Green	—	1777, 1673 <sup>d</sup>	IR (79)	(79)
CpCr(NO) <sub>2</sub> CH <sub>2</sub> Cl	Green	71°	1779, 1704 <sup>d</sup>	IR (79)	(79)
CpCr(NO) <sub>2</sub> ( $\pi$ -C <sub>3</sub> H <sub>5</sub> )	Brown	67°	1787, 1685 <sup>d</sup>	IR (79)	(79)
CpCr(NO) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> )	Green	—	1790, 1685 <sup>d</sup>	IR (79)	(79)
[CpCr(NO) <sub>2</sub> (CO)]PF <sub>6</sub>	Green	—	1873, 1779 (2137) <sup>e</sup>	IR (20)	(20)
[CpCr(NO) <sub>2</sub> (PPh <sub>3</sub> )] <sup>+</sup>	—	—	—	—	(48)
Cp <sub>2</sub> Cr <sub>2</sub> (NO) <sub>4</sub>	Purple	158°	1672, 1505 <sup>b</sup>	IR (58) EL (58) NMR (58)	(58, 78)
Cp <sub>2</sub> Cr <sub>2</sub> (NO) <sub>2</sub> XX (X = Z = SMe, SPh, OMe, NMe <sub>2</sub> ; X = SMe, Z = OH)	—	—	—	M (82)	(82)
CpMo(NO)(CO) <sub>2</sub>	Orange	85°	1678 (2015, 1940, 1910) <sup>h</sup>	IR (79)	(57, 79)
CpMo(NO)I <sub>2</sub> (PPh <sub>3</sub> )	—	—	1660 <sup>e</sup>	IR (57) EL (57) NMR (57)	(57)

CpMo(NO)I <sub>2</sub> (P(OPh) <sub>3</sub> )	—	—	1679 <sup>e</sup>	IR (57) EL (57) NMR (57)	(57)
CpMo(NO)I <sub>2</sub> py	—	—	1661 <sup>e</sup>	IR (57) EL (57) NMR (57)	(57)
CpMo(NO)I <sub>2</sub> bipy	—	—	1674 <sup>e</sup>	IR (57) EL (57) NMR (57)	(57)
Cp <sub>2</sub> Mo <sub>2</sub> (NO) <sub>2</sub> I <sub>4</sub>	Purple	250° dec	1670 <sup>e</sup>	IR (57) M (57)	(57)
CpW(NO)(CO) <sub>2</sub>	—	—	—	—	(19)
[CpMn(NO)(CO) <sub>2</sub> ]PF <sub>6</sub>	Yellow	230° dec	1840 (2125, 2075) <sup>e</sup>	IR (58) NMR (58) POL (16)	(51, 81)
CpMn(NO)(CO)(MeCOO)	Orange	56°	1786 (2023) <sup>a</sup>	IR (59) NMR (59)	(59)
CpMn(NO)(CO)(MeCO)	Brown	−15°	1730 (1990) <sup>k</sup>	IR (59)	(59)
Cp <sub>2</sub> Mn <sub>2</sub> (NO) <sub>2</sub> (CO) <sub>2</sub>	Red	200° dec	1707, 1509 (1956, 1781) <sup>e</sup>	IR (58) NMR (58) POL (16)	(58)
Cp <sub>3</sub> Mn <sub>2</sub> (NO) <sub>3</sub>	Red	—	1720, 1497 <sup>e</sup>	IR (58) NMR (58) POL (16) X (17a)	(17a, 58, 78)
Cp <sub>3</sub> Mn <sub>3</sub> (NO) <sub>4</sub>	Black	—	1543, 1481, 1328 <sup>d</sup>	IR (17a) NMR (58)	(58)
[CpMn(NO) <sub>2</sub> ] <sub>n</sub>	Black	—	1760, 1525 <sup>e</sup>	IR (57) NMR (57)	(57)
[CpMn(NO)S <sub>2</sub> ] <sub>n</sub>	Brown	—	1743 <sup>e</sup>	IR (80) X (17a)	(80)
Co(NO) <sub>2</sub> (C <sub>2</sub> F <sub>5</sub> )(PPh <sub>3</sub> )	Violet	65°	1829, 1774 <sup>d</sup>	IR (40)	(40)
Co(NO) <sub>2</sub> (CF <sub>3</sub> )[P(OPh) <sub>3</sub> ]	Red	58°	1848, 1789 <sup>d</sup>	IR (41)	(41)
Co(NO) <sub>2</sub> (C <sub>2</sub> F <sub>5</sub> )[P(OPh) <sub>3</sub> ]	Red	59°	1850, 1792 <sup>d</sup>	IR (41)	(41)
Co(NO) <sub>2</sub> (C <sub>3</sub> F <sub>7</sub> )[P(OPh) <sub>3</sub> ]	Red	54°	1850, 1792 <sup>d</sup>	IR (41)	(41)
CpNi(NO)	Red	−41° (b.p. 144°)	1810 <sup>k</sup>	IR (18) MIC (13) M (23a)	(56, 81)
CpPd(NO)	—	−30°	1759 <sup>e</sup>	IR (23) NMR (23)	(23)
CpPt(NO)	—	64°	—	IR (22)	(22)

\* See footnotes to Table II.



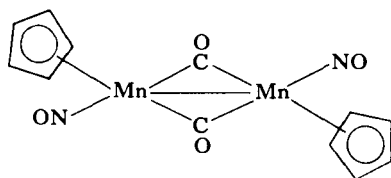
(IV)



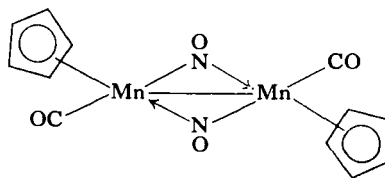
(V)

A broad band appears at  $1497\text{ cm}^{-1}$  in the infrared spectrum of this complex, and is ascribed to the bridging N—O stretch, while the terminal N—O stretch appears at  $1720\text{ cm}^{-1}$ .

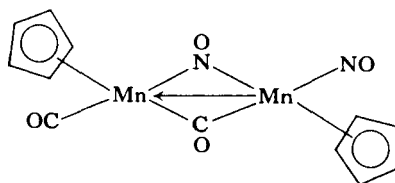
Infrared spectra suggest that  $[\text{CpMn}(\text{CO})(\text{NO})]_2$ , made by reduction of salts of  $[\text{CpMn}(\text{NO})(\text{CO})_2]^+$  with sodium borohydride, may have structures (VI), (VII), or (VIII), or indeed that the product may be an equilibrium mixture of the three types (58).



(VI)



(VII)



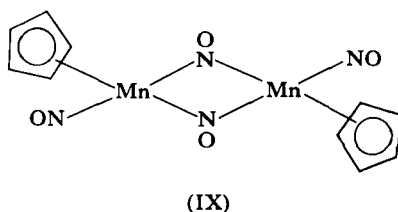
(VIII)

Irradiation of a solution of the complex in benzene with ultraviolet light gives a black diamagnetic species which was formulated as  $\text{Cp}_6\text{Mn}_6(\text{NO})_8$  (58). However, as described in an earlier section, this compound has the molecular formula  $\text{Cp}_3\text{Mn}_3(\text{NO})_4$  (17a).

Irradiation of a solution of sodium nitrite and  $[\text{CpMn}(\text{NO})(\text{CO})_2]\text{PF}_6$  with ultraviolet light yields a black product of composition  $[\text{CpMn}(\text{NO})_2]_n$ ; the value of  $n$  could not be determined (57).

Finally, treatment of a solution of  $\text{CpCr}(\text{NO})_2\text{Cl}$  with borohydride yields  $[\text{CpCr}(\text{NO})_2]_2$  as red-violet crystals. On the basis of the infrared

spectrum of the complex, and its chemical similarity to the isoelectronic  $[\text{CpFe}(\text{CO})_2]_2$ , structure (IX) was proposed.



The terminal N—O stretch is at  $1672\text{ cm}^{-1}$ , and the bridging band is at  $1505\text{ cm}^{-1}$  (58). The structure is somewhat similar to that proposed for  $\text{Cp}_3\text{Mn}_2(\text{NO})_3$  and for  $[\text{CpMn}(\text{NO})(\text{CO})]_2$ , this latter complex being isoelectronic with  $[\text{CpCr}(\text{NO})_2]_2$ .

### E. Miscellaneous Organometallic Nitrosyls

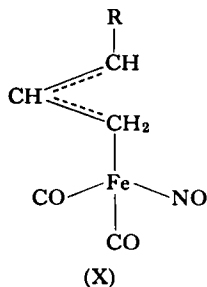
A number of these complexes are listed in Tables II and IV.

#### 1. Alkyl and Perfluoroalkyl Species

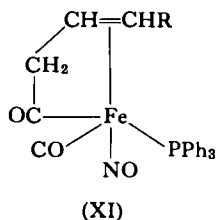
The alkyl complexes  $\text{CpCr}(\text{NO})_2\text{R}$  ( $\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{Cl}, \sigma\text{-C}_5\text{H}_5, \text{Ph}$ ) have already been mentioned. The perfluoroalkyl complexes  $\text{Co}(\text{NO})_2\text{R}_\text{F}[\text{P}(\text{OPh})_3]$  ( $\text{R}_\text{F} = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7$ ) and  $\text{Co}(\text{NO})_2(\text{C}_2\text{F}_5)(\text{PPh}_3)$  have been prepared by the action of nitric oxide on the isoelectronic carbonyls,  $\text{Co}(\text{CO})_3\text{R}_\text{F}[\text{P}(\text{OPh})_3]$  and  $\text{Co}(\text{CO})_3\text{R}_\text{F}(\text{PPh}_3)$ , respectively (40, 41). The perfluoroacetyl species  $\text{Fe}(\text{NO})(\text{CO})\text{R}_\text{F}(\text{PPh}_3)_2$  ( $\text{R}_\text{F} = \text{CF}_3\text{CO}, \text{C}_2\text{F}_5\text{CO}$ ) have also been made from the corresponding acids and  $\text{Fe}(\text{NO})_2(\text{CO})_2$  (37). The alkoxy complexes  $\text{CpMn}(\text{NO})(\text{CO})(\text{MeCOO})$ , obtained from  $[\text{CpMn}(\text{NO})(\text{CO})_2]^+$  and sodium methoxide, and  $\text{CpMn}(\text{NO})(\text{CO})(\text{MeCO})$ , prepared from the acetyl complex and methylmagnesium bromide, have recently been reported (59).

#### 2. $\pi$ -Allyl Complexes

Treatment of  $(\pi\text{-RCHCH=CH}_2)\text{Fe}(\text{CO})_3$  ( $\text{R} = \text{H}, \text{Me}, \text{MeCO}$ ) with nitric oxide yields the isoelectronic nitrosyls  $(\pi\text{-RCHCH=CH}_2)\text{Fe}(\text{NO})(\text{CO})_2$  (8, 72) (see Table II). The proton magnetic resonance spectra of these suggest structure (X) for these compounds.



In the case of  $R = \text{MeCOO}$  the proton magnetic resonance spectrum suggests that the proton adjacent to the ester group is anti and the ester group syn with respect to the proton at the apex of the allyl group (72). Treatment of the allyls (with  $R = \text{H}$  or  $\text{Me}$ ) with triphenylphosphine gives  $\text{Fe}(\text{NO})(\text{CO})-(\pi\text{-RCHCH=CH}_2)(\text{PPh}_3)$ . An acyl species of type (XI)



is also formed during the reaction (8).

### 3. Tricyanomethanide Complexes

Treatment of potassium tricyanomethanide with  $[\text{Co}(\text{NO})_2\text{Cl}]_2$  or  $[\text{Ni}(\text{NO})\text{I}]_4$  yields the polymers  $\{\text{Co}(\text{NO})_2[\text{C}(\text{CN})_3]\}_n$  and  $\{\text{Ni}(\text{NO})[\text{C}(\text{CN})_3]\}_n$ , respectively. These species, thought to contain  $\text{C}(\text{CN})_3$  bridges, react with phosphines to give  $\text{Co}(\text{NO})_2(\text{PR}_3)[\text{C}(\text{CN})_3]$  and  $\text{Ni}(\text{NO})(\text{PR}_3)_2[\text{C}(\text{CN})_3]$  ( $R = \text{Ph}$ ,  $\text{C}_6\text{H}_{11}$ ). Other complexes prepared were  $\{\text{Ni}(\text{NO})(\text{PR}_3)[\text{C}(\text{CN})_3]\}$  and  $\text{Ni}(\text{NO})[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2][\text{C}(\text{CN})_3]$  (4).

## V

### PHYSICAL DATA

Apart from the structural studies already mentioned, a number of other measurements, particularly of infrared spectra, have been made on organo-metallic nitrosyls.

### A. Infrared Spectra

In most nitrosyl complexes the N—O stretching frequency is observed as an intense and characteristic band in the region  $1550\text{--}1950\text{ cm}^{-1}$ , and such bands are associated with monodentate nitrosyl groups. Assuming the nitrosonium coordination model, the free  $(\text{NO})^+$  stretching frequency of  $2250\text{ cm}^{-1}$  [as found in nitrosonium salts of the type  $\text{NO}^+(\text{SbCl}_6)^-$ ] would be expected to drop on coordination with a metal atom, the magnitude of the drop depending on the nature of the metal atom and the degree of  $\sigma$ - and  $\pi$ -bonding involved.

Although it has been suggested that N—O stretching frequencies in the  $1515\text{--}1700\text{ cm}^{-1}$  region are diagnostic of bent M—N—O systems (24) there is as yet absolutely no evidence for this. The wide variation in N—O stretches is rather to be associated with (a) the oxidation state and coordination number of the metal atom and (b) the  $\pi$ -acceptor and  $\sigma$ -donor abilities of the other ligands present. The profound effect of (a) is apparent from the wide range of values found for nitrosyl pentacyano complexes (see Table III). While the presence of intense bands in the  $1550\text{--}1950\text{ cm}^{-1}$  region may be used as diagnostic of the presence of a terminal N—O group, it is found that bridging N—O groups have N—O stretches at lower frequencies, around  $1450\text{ cm}^{-1}$ , or even as low as  $1328\text{ cm}^{-1}$ , in  $\text{Cp}_3\text{Mn}_3(\text{NO})_4$ . A similar drop in frequency is observed from terminal to bridging carbonyl groups. It appears that the more metal atoms bridged by a CO or NO group the lower is the observed stretching frequency of CO or NO.

As yet there is little information available on the frequency of the metal–nitrogen stretching and M—N—O deformation modes in nitrosyl complexes. Such data as appertain to the organometallic species are listed in Table V. It should be noted that, with the possible exception of the data for  $\text{Co}(\text{NO})(\text{CO})_3$ , for which isotopic substitution results are available, there is no certain way of distinguishing between the M—N stretch and the M—N—O bend in metal nitrosyls from infrared data alone, and this problem is likely to remain unresolved until Raman data are available on such complexes.

There have been a number of studies on shifts of  $\nu_{\text{N—O}}$  in complexes dissolved in a variety of organic solvents (6a, 46, 47), and the results have been interpreted in terms of slight changes of electron density around the metal atom brought about by using solvents of varying polarity and polarizability. For  $\text{Co}(\text{NO})(\text{CO})_3$ , for example,  $\nu_{\text{N—O}}$  appears at  $1805\text{ cm}^{-1}$  in isoamyl alcohol solution and at  $1791\text{ cm}^{-1}$  in methylene iodide, this



TABLE V  
INFRARED DATA FOR ORGANOMETALLIC NITROSYLS<sup>a</sup>

Complex	$\nu_{\text{N—O}}$	$\nu_{^{15}\text{N—O}}$	$\nu_{\text{M—N}}$	$\nu_{\text{M—}^{15}\text{N}}$	$\delta_{\text{M—N—O}}$	$\delta_{\text{M—}^{15}\text{N—O}}$	References
$\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$	1630vs	—	616m	—	?616m	—	25
$\text{K}_3[\text{Mn}(\text{NO})(\text{CN})_5]$	1700vs	—	655m	—	?655m	—	25
$\text{K}_2[\text{Mn}(\text{NO})(\text{CN})_5]$	1885vs	—	622s	—	—	—	68
$\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5] \cdot 2 \text{H}_2\text{O}$	1929vs	—	650m	—	662m	—	86a
	1910s						
$\text{K}_2[\text{Ru}(\text{NO})(\text{CN})_5]$	1915vs	—	633m	—	420w	—	17
$\text{Co}(\text{NO})(\text{CO})_3$ <sup>b</sup>	1822vs	1786vs	594m	591m	565m	555m	64
$\text{K}_3[\text{Co}(\text{NO})(\text{CN})_5]$	1150m	1119m	—	—	—	—	32
$\text{CpNi}(\text{NO})$ <sup>c</sup>	1810vs	—	640m	—	570vw	—	18

<sup>a</sup> Spectra measured on solid samples except where noted. Frequencies in  $\text{cm}^{-1}$ .

<sup>b</sup> Spectrum measured on gas.

<sup>c</sup> Spectrum measured on liquid.

representing the widest range of frequencies observed with any pair of organic solvents (46). Detailed studies have been carried out on the variation of  $\nu_{\text{N-O}}$  values in a wide range of substituted iron and cobalt nitrosyl carbonyl complexes as other ligands are varied, but data on metal-nitrogen stretches were not obtained (6, 47). It appeared from these studies that the nitrosyl ligand is a more efficient  $\pi$ -acceptor than the carbonyl group (6, 47). The ratio of absolute intensities of symmetric and asymmetric N—O and C—O stretches in substituted and unsubstituted iron and cobalt nitrosyl carbonyls has been used to calculate bond angles in the complexes (6a).

No Raman measurements have as yet been reported on nitrosyl complexes, due to their colors and ease of decomposition, but the advent of laser sources will no doubt stimulate research in this area.

### *B. Electronic Absorption Spectra*

Most of the studies of electronic spectra have been confined to the nitrosyl pentacyano species, though there are some data available on other systems (see Tables II and IV). For the nitrosyl pentacyanides (Table III) the observed spectra have been interpreted on the basis of the molecular orbital scheme of Manoharan and Gray (68), following self-consistent charge and configurational molecular orbital calculations. The very strong M—NO bond is considered to dominate the overall ligand field (68). Single-crystal, low-temperature spectra of  $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$  with polarized light have been measured (68).

### *C. Magnetic Measurements*

These have been few for organometallic nitrosyls since only the nitrosyl pentacyanides show paramagnetism. The susceptibility of  $\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_5] \cdot \text{H}_2\text{O}$  has been measured over the range  $85^\circ$ – $296^\circ$  K and the values  $\mu_{\text{eff}} = 1.87$  BM and  $\theta = -7^\circ$  obtained (30). This moment is consistent with the presence of one unpaired spin per chromium atom in accordance with the formulation of the complex as containing chromium(I). The susceptibility of  $\text{Zn}[\text{Mn}(\text{NO})(\text{CN})_5]$  in the solid state was measured over the temperature range  $74^\circ$ – $300^\circ$  K and values of  $\mu_{\text{eff}} = 1.86$  BM and  $\theta = -6.3^\circ$  obtained. Curiously, the solid potassium and silver salts have much lower moments (0.50 and 0.55 BM at room temperatures), but an acetone solution of the potassium salt gave a moment of 1.76 BM at  $300^\circ$  K (12). Susceptibility

measurements on an aqueous solution of the  $[\text{Fe}(\text{NO})(\text{CN})_5]^{3-}$  ion, made by treating acid solutions of  $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$  with nitric oxide, suggest that this has one unpaired spin per iron atom (28), but this species does not appear to be identical with the product of a one-electron electrolytic reduction of  $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$  (45).

#### D. Electron Spin Resonance

Here again measurements are confined to the nitrosyl pentacyanides. There is a large literature on the ESR spectrum of  $\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_5]$  (48, 68, 71; and references therein) and some disagreement as to the interpretation, but the formulation of the complex as a nitrosonium coordination compound is upheld by the results, and this is also the conclusion reached from ESR studies on the isoelectronic complex  $\text{K}_2[\text{Mn}(\text{NO})(\text{CN})_5]$  (68). In the case of  $[\text{Fe}(\text{NO})(\text{CN})_5]^{3-}$ , a species not yet isolated from solution, the delocalization of the unpaired electron onto the ligand appears to be such that the complex may almost be regarded as an example of nitric oxide donating an electron pair only to iron(II) (45). A study of  $^{13}\text{C}$  hyperfine interaction in the ion has recently been made (15).

#### E. Proton Magnetic Resonance

Spectra have been measured for a number of organometallic nitrosyls and in some cases the results have helped in assignment of structures, notably in the cases of cyclopentadienyl and allyl nitrosyls. References are given in Tables II and IV.

#### F. Mössbauer Spectra

Measurements have been made on  $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$ , and are consistent with the presence of a strongly  $\pi$ -accepting coordinated nitrosonium group (14).

#### G. Mass Spectra

Mass spectra have been measured of complexes of the form  $\text{Cp}_2\text{Cr}_2(\text{NO})_2\text{XZ}$ , where X and Z are bridging groups ( $\text{X}=\text{Z}=\text{SMe}$ ,  $\text{SPh}$ ,  $\text{OMe}$ ,  $\text{NPh}_2$ ;  $\text{X}=\text{SMe}$ ,  $\text{Z}=\text{OH}$ ); the nitrosyl groups are removed first from the molecule (82). Mass spectra have also been measured for the following

nitrosyls (ionization potentials in electron volts given in parentheses):  $\text{Co}(\text{NO})(\text{CO})_3$  (8.75);  $\text{Co}(\text{NO})(\text{CO})_2(\text{PCl}_3)$  (8.40);  $\text{Fe}(\text{NO})_2(\text{CO})_2$  (8.45);  $\text{Fe}(\text{NO})_2(\text{CO})[\text{P}(\text{OEt})_3]$  (7.50);  $\text{CpNi}(\text{NO})$  (8.50). These results were correlated with the supposed  $\sigma$ - and  $\pi$ -bonding tendencies of the ligands involved (23a).

### H. Dipole Moments

The data available on organometallic nitrosyls are summarized in Table VI. Dipole moments are useful in establishing the molecular configurations of some of the individual complexes. Thus, the low moments observed for  $\text{Mn}(\text{NO})(\text{CO})_2(\text{PPh}_3)_2$  and  $\text{Mn}(\text{NO})(\text{CO})_2[\text{P}(\text{C}_6\text{H}_{11})_3]_2$  have been used as evidence that these monomeric species have a trigonal bipyramidal structure with the phosphine groups occupying the trans axial positions in the molecule (44).

### I. Kinetics and Mechanism

The carbonyl replacement reaction between  $\text{Co}(\text{NO})(\text{CO})_3$  and a variety of ligands L (phosphines, phosphites, pyridines, and isonitriles) to give  $\text{Co}(\text{NO})(\text{CO})_2\text{L}$  has been studied. The reactions are fast with phosphines

TABLE VI  
DIPOLE MOMENTS FOR ORGANOMETALLIC NITROSYLS

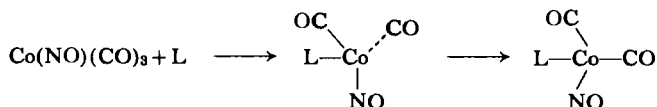
Complex	Dipole moment <sup>a</sup> (debyes)	References
$\text{CpCr}(\text{NO})(\text{CO})_2$	$3.2 \pm 0.03$	97
$\text{Mn}(\text{NO})(\text{CO})_2(\text{PPh}_3)_2$	$0.52 \pm 0.5$	44
$\text{Mn}(\text{NO})(\text{CO})_2[\text{P}(\text{C}_6\text{H}_{11})_3]_2$	$0.75 \pm 0.3$	44
$\text{Mn}(\text{NO})(\text{CO})_3(\text{PPh}_3)$	$4.93 \pm 0.05$	44
$\text{Mn}(\text{NO})(\text{CO})_3[\text{P}(\text{C}_6\text{H}_{11})_3]$	$5.26 \pm 0.06$	44
$\text{Fe}(\text{NO})_2(\text{CO})_2$	$0.95 \pm 0.06$	97
$\text{Fe}(\text{NO})_2(p\text{-MeOC}_6\text{H}_4\text{NC})_2$	6.52	67
$\text{Fe}(\text{NO})_2(p\text{-MeC}_6\text{H}_4\text{NC})_2$	6.09	67
$\text{Co}(\text{NO})(\text{CO})_3$	$0.72 \pm 0.06$	97
$\text{Co}(\text{NO})(p\text{-MeC}_6\text{H}_4\text{NC})_3$	5.29	67
$\text{Co}(\text{NO})(p\text{-ClC}_6\text{H}_4\text{NC})_3$	3.33	67
$\text{Co}(\text{NO})(p\text{-MeOC}_6\text{H}_4\text{NC})_3$	5.78	67
$\text{Ir}(\text{NO})(\text{CO})(\text{PPh}_3)_2$	6.75	2

<sup>a</sup> Measured in benzene solutions at 25° C.

and phosphites and slow with arsines or pyridine, consistent with the class (b) character of the substrate. For many of these nucleophiles the rate law

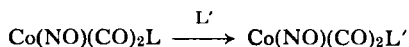
$$\text{rate} = k_2[\text{Co}(\text{NO})(\text{CO})_3][\text{L}]$$

is followed, suggesting a bimolecular displacement mechanism



It has been suggested that such a mechanism would be facilitated by a transition state in which the nitric oxide functions as the  $\text{NO}^-$  ligand, thus leaving a vacant, low-energy orbital on the metal. The influence of such other factors as  $\pi$ -bonding, ligand basicity, and solvent character have also been discussed (90). The exchange of  $^{14}\text{CO}$  with  $\text{Co}(\text{NO})(\text{CO})_3$  has also been studied. In toluene solutions it is slow and takes place by a first-order process, zero-order in  $(\text{CO})$  (96). Preliminary data on the reaction of triphenylphosphine with  $\text{Mn}(\text{NO})(\text{CO})_4$  have been reported (17a).

Kinetics of the following process have been studied:



where  $\text{L} = \text{CO}$ ,  $\text{C}_6\text{H}_{11}\text{NC}$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ ,  $\text{AsPh}_3$ ;  $\text{L}' = \text{PPh}_3$ ,  $\text{PPh}_2\text{Et}$ ,  $\text{P}(n\text{-C}_4\text{H}_9)_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OPh})_3$ , and the results compared with those obtained for the  $\text{Ni}(\text{CO})_2\text{L}_2$  system (91).

Kinetics of the reactions between  $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$  and hydrogen sulfide (85); hydroxide ion (88) and propane; and butane and 3-pentanone in the presence of hydroxide have recently been reported (89).

### J. Polarography

Polarographic reduction of a few organometallic nitrosyls has been studied (see Tables III and IV).

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# Recent Developments in the Organic Chemistry of Lead: Preparations and Reactions of Compounds with Pb—C, Pb—H, Pb—N, and Pb—O Bonds

W. P. NEUMANN AND K. KÜHLEIN<sup>1</sup>

*Institute of Organic Chemistry  
Justus Liebig University  
Giessen, Germany*

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<sup>1</sup> *Present address:* Farbwerke Hoechst A.G., Frankfurt/Main, Germany.

## I

## INTRODUCTION

*A. Historical Aspects, Limits of the Topic*

While the chemistry of organic compounds of germanium (227) and tin (189) has developed at a rapid pace during the past 20 years, there has been little research on the organic compounds of the next higher element of Group IV, lead, until very recently. For instance, in the tabular review of Dub (52), which covers the literature up to the end of 1964, almost two-thirds (61 %) covers the organic compounds of tin, one-fourth (26 %) those of germanium, and only 13 % those of lead.

The development of the chemistry of organic lead compounds can be divided into three stages. Following the preparation of the first alkyllead compound, hexaethyldiplumbane, in 1853 by Löwig (171), attention was focused on the concept of valence and also the development of the structural theory of organic chemistry, mainly in view of early theories of radicals. Then in 1929 Paneth and collaborators (214, 215), in their classical experiment with tetramethyllead and tetraethyllead, were able to prove beyond doubt the existence of short-lived free radicals, long before anything was known of electron spin resonance spectroscopy.

Later interest was concentrated on alkyllead compounds themselves. The preparations of the separate types  $R_4Pb$ ,  $R_3PbX$ ,  $R_2PbX_2$ ,  $RPbX_3$ , and  $R_3Pb-PbR_3$  were systematically studied. R represented almost exclusively simple aromatic or aliphatic substituents without functional groups, and X represented negative substituents, i.e., halogen or  $-OCOR$ , or also metals, i.e., lithium. From this "classical preparative" period only the excellent results of Grüttner, Krause, and their collaborators during the years 1915–1936 (149) and of the group of Gilman (161) will be mentioned here. During this period Midgley and collaborators (69, 182) discovered tetraethyllead as an antiknock agent for gasoline, which led to enormous industrial production. Tetraethyllead together with the tetramethyl derivative, which is now being used for the same purpose, are still by far the organometallic compounds produced in largest amount.

During the past few years the interests of research chemists have shifted more toward questions of the theory of bonding and structure, the mechanisms of known reactions, and the evaluation of new reaction possibilities. Previously known organolead compounds, as for instance those with  $Pb-O$  groups, were suddenly found to have many new uses as reaction

participants, and to these were added new alkyllead compounds with Pb—N and Pb—H groups. Also the Pb—C bond has been shown to be more reactive than was previously thought. The main interest today in organolead research is centered on the use of alkyllead compounds as intermediates in the synthesis of new organic and organometallic compounds.

The borders between the three stages are, of course, not sharp and even today the improvement of methods of preparation for simple lead alkyls such as tetraethyllead or tetrabutyllead is of great importance. But the following remarks are meant to deal mainly with the third and newest part of the development. This decision is an easy one because the developments until 1936 (149), until 1952 (161), and to the middle of 1963 (273, 274) are treated in excellent reviews. Also there are critical reports on some topics, for instance, "Catenated Organic Compounds of ... Pb" (77), redistribution reactions (185, 190), molecular complexes (76), and sulfur-containing alkyllead compounds (1). The literature up to 1964 has been compiled by Dub (52). For 1964, 1965, and 1966 annual surveys (250) are available.

Moreover, the applications of alkyllead compounds cannot be discussed in detail here. We refer to the new reviews on this topic (52, 134, 136), especially to the recent and important possibilities of applications such as biocides (52, 134), and further to the current reports of industrial organizations (121). This review is concerned with the recent advances in the chemistry of Pb—C, Pb—H, Pb—N, and Pb—O compounds, and deals mainly with their application to synthesis in organic chemistry. It considers publications which have appeared up to September 1967, or those which are referred to in *Chemical Abstracts*. This review is selective; a complete listing of the previous literature can be found in the above-mentioned reviews.

### ***B. Structure and Reactivity of Organic Lead Compounds***

In nearly all of its organic compounds the lead atom possesses  $sp^3$  hybridization; it forms four covalent bonds for which the tetrahedral model is valid. An exception is the dicyclopentadienyllead, which has delocalized  $\sigma$ -bonds and an angular sandwichlike structure (8, 64). Today there is no proof for the existence of monomeric compounds like  $R_2Pb$  with localized  $\sigma$ -bonds. But it could be that highly reactive short-lived intermediates can have localized  $\sigma$ -bonds.

TABLE I<sup>a</sup>  
SOME PHYSICAL DATA OF GROUP IVB M—C, M—H, AND M—M BONDS

M	Electronegativity (7)	Covalent radius (Å)	Length of bonds		Energy of dissociation		
			M—C (Å)	M—H <sup>b</sup> (Å)	M—C (38, 254, 261)	M—H (157, 191, 254, 261)	M—M (228, 254, 261)
C	2.60	0.77	1.54	1.07	87	89	80
Si	1.90	1.18	1.95	1.48	65	74	74 (51)
Ge	2.00	1.22	1.99	1.52	60	69	64 (51)
Sn	1.93	1.40	2.17	1.70	47	35–50 (157, 191)	46–50 (51, 228)
Pb	2.45	1.52	2.29	1.82	31	23 <sup>c</sup>	23 (51)

<sup>a</sup> Further discussion in Cottrell (38), Skinner (254), Stone (261), and Sutton (263).

<sup>b</sup> Calculated from the covalent radius of hydrogen and of the elements of Group IVB.

<sup>c</sup> Estimation from the value of Pb—Pb and from our own experience.

The orbitals of the lead atom up to and including  $4f$  are fully occupied. Then follows the arrangement  $5s^25p^65d^{10}6s^26p^2$ . Empty orbitals can be used for the formation of stable complexes (review 76) and for the formation of short-lived transition states. Utilization of these empty orbitals is largely responsible for the reactivity and the considerable number of different types of reactions of organic lead compounds. Of all the elements of Group IVB, lead has the largest covalent radius. This leads to a small amount of shielding of the lead atom by substituents, large interatomic distances, and correspondingly small bonding energies. Lead is more electronegative than the elements Si, Ge, and Sn if one considers the  $sp^3$  hybridization which is characteristic of organolead compounds (7); see Table I.<sup>2</sup> Therefore, the polarity of M—C and M—H bonds in organolead compounds is relatively small, but their polarizability is quite considerable. In Group IVB Pb—C and Pb—H bonds have the greatest reactivity and smallest thermal stability towards both polar and radical reagents. These facts must always be considered in connection with the synthesis and reactions of organolead compounds (see Table I).

## II

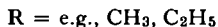
### THE Pb—C BOND

#### A. Lead Tetraalkyls without Functional Groups

##### 1. Preparation

There are three important procedures:

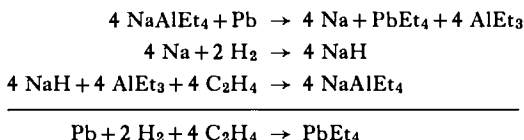
(1) The alkylation of lead-alkali metal alloys with alkyl halides is the oldest (171) and probably even today the most widely used procedure in industry (14). Many different agents have been found to catalyze these reactions quickly and smoothly (252).



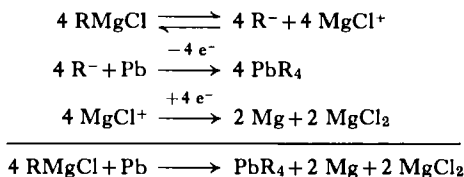
(2) Ziegler and collaborators (162, 283) succeeded in the electrolytic preparation of tetraethyllead, a process which is also suitable for obtaining other ethyl metal compounds. The electrolysis of alkali aluminum (or boron) tetraethyl with a lead anode and a mercury cathode yields at the anode a

<sup>2</sup> Other tables of electronegativities are related to the cations of the elements (review in Neumann, 189) and should not be used here for comparison.

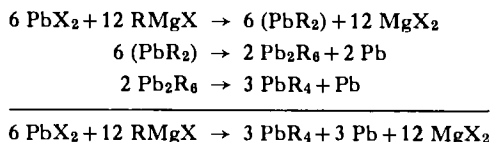
mixture of tetraethyllead and triethylaluminum (or triethylboron). The sodium formed on the cathode can be transformed into NaH and the electrolyte can be regenerated. Thus the overall result is a synthesis of  $\text{Pb}(\text{Et})_4$  from Pb,  $\text{H}_2$ , and  $\text{C}_2\text{H}_4$ .



This synthesis has several advantages compared to procedure (1), in that the NaCl electrolysis, the preparation of EtCl, the preparation of lead-sodium alloys, and regeneration of the nonreacted lead are not necessary. Also, in the electrolytical process the yield based on the amount of lead consumed is practically 100%. Recently the Nalco Chemical Company (13, 28, 30) has worked out a process for  $\text{Pb}(\text{Me})_4$  and  $\text{Pb}(\text{Et})_4$  in which the corresponding Grignard compound is electrolyzed at a lead anode. The Grignard compound is regenerated utilizing the Mg precipitated on the cathode and by simultaneously adding alkyl chloride.

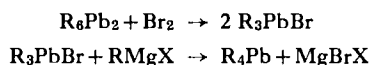


(3) Methods (1) and (2) are large-scale processes. In the laboratory the starting materials are without exception lead(II) compounds, mainly lead(II) chloride, which are reacted with suitable alkylating agents such as organic compounds of magnesium, lithium, aluminum, and boron. Thereby dialkyl and diaryl lead compounds are probably formed as unstable intermediates, which spontaneously disproportionate, respectively, via the hexaalkyl or hexaaryl diplumbanes to the desired tetraalkyl (aryl) compounds.



Depending on the substituents ( $\text{R} = \text{C}_2\text{H}_5$ ) and reaction conditions, the reaction may proceed to completion, or may partially stop at the diplumbane

stage. In these cases, as for the preparation of *n*-Bu<sub>4</sub>Pb, it is necessary to add a solution of bromine in hexane to the reaction mixture at  $-80^{\circ}\text{C}$  until all of the diplumbane has been converted to R<sub>3</sub>PbBr. The end point of the reaction is recognized when the yellow reaction mixture turns colorless. After filtering to remove unreacted PbBr<sub>2</sub> and any R<sub>2</sub>PbBr<sub>2</sub>, the resulting mixture, which consists mainly of R<sub>3</sub>PbBr and a small amount of R<sub>4</sub>Pb, is again alkylated. The resulting R<sub>4</sub>Pb, completely free of diplumbane, can be distilled without difficulty under vacuum if R = C<sub>4</sub>H<sub>9</sub> (154).



The use of lead(IV) compounds such as the difficultly available PbCl<sub>4</sub> or K<sub>2</sub>PbCl<sub>6</sub>, to avoid the Pb separation is generally useless since both are strong oxidizing agents and in the presence of organometallic compounds are easily transformed to the lead(II) derivatives. Further details about all three procedures can be found in the literature (52, 149, 161, 250, 273, 274).

## 2. Reactions

Because of the polarizability and relatively small dissociation energy, the Pb—C bond takes part in many reactions. While the lead tetraalkyls are only slowly attacked by light, water, or oxygen under normal conditions, ozone cleaves one or two ethyl groups from Et<sub>4</sub>Pb smoothly at  $-68^{\circ}\text{C}$  (6). Ultraviolet light homolyzes Pb—C bonds even at  $20^{\circ}\text{C}$ , e.g., in cyclohexyllead compounds (132). Heating at  $150^{\circ}\text{C}$  results in a homolytic cleavage of the Pb—C bond, forming free radicals (183, 222, 233, 234). These are capable of causing polymerization of added unsaturated compounds (140, 179, 273) and of isomerizing a mixture of two lead tetraalkyl compounds to a statistical equilibrium (33).

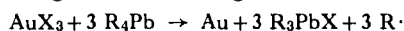
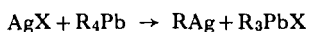
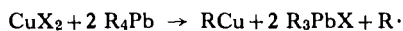


Similar "redistribution reactions" in the presence of Lewis acids take place at room temperature (32–34). This is of technical significance (Me<sub>4</sub>Pb + Et<sub>4</sub>Pb). The classical papers by Calingaert *et al.* (32–34) and some recent results are reviewed by Moedritzer (185). Besides radical reactions, polar reactions of the Pb—C bond can often be observed, i.e., cleavage with acids, halogens, and alkali metals (79, 110, 149, 161, 242).

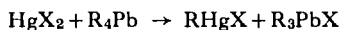
Mechanisms of reactions of the Pb—C bond have been established in detail only in few cases, insofar; e.g., different types of S<sub>E</sub> mechanisms are

effective on carbon for cleavage of  $R_4Pb$  with some halogens and acids (3).

According to the reaction conditions one or more of the organic substituents are cleaved. These reactions are of importance mainly for the synthesis of organolead salts, since comproportionation reactions in organolead chemistry have until now been of no significant importance (138, 159, 185). The  $Pb-C$  bond is also cleaved by hydrogen (74), oxygen (photooxidation) (5), liquid ammonia (247), sulfur (116),  $SO_2$  (71, 117),  $SO_3$  (72), benzoyl peroxide (211, 231), and halogenated methanes (177, 230, 258). Its reactivity towards metal and nonmetal halides of cobalt, iron, manganese, titanium (226, 232), sulfur (70), and phosphorus (286) have been investigated many times in the past years, and all are found to cleave organic groups at higher temperature. Also selenium diselenocyanate is capable of cleavage (17). The reactions with the halides of copper, silver, gold (22, 23, 37, 94, 235, 257, 265), mercury (272), and germanium (155, 184) as well as mercury nitrate (264) are useful preparatively. Copper, silver, and gold salts are alkylated at  $-80^\circ C$  first. But, these metal alkyls decompose partly, forming free radicals  $R\cdot$ .



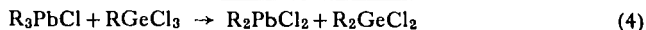
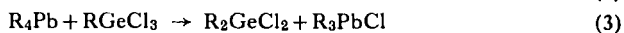
Mercury(II) salts are alkylated to the  $RHgX$  compounds.



$GeCl_4$  undergoes a slow reaction at room temperature, while at  $100^\circ C$  complete reaction takes place rapidly [Eq. (1)].

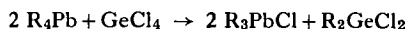


At higher temperatures a second alkyl group is transferred to germanium (4). Diethylgermanium dichloride is thus formed quantitatively from  $GeCl_4$  and tetraethyllead. The reaction mixture is heated first to  $90^\circ C$  [Eq. (1)] and afterwards to  $140^\circ C$  [Eq. (4)]. Probably not only the initially formed triethyllead chloride [Eq. (1)] serves as a further alkylating agent, but also tetraethyllead [Eq. (3)] which is formed at this temperature by disproportionation according to [Eq. (2)] (34).

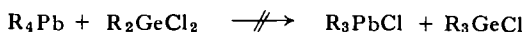




With R = butyl or isobutyl, reaction (4) takes place very slowly (i.e., 10% after 80 hours at 140° C), because the thermally stable butyllead compounds are inert towards disproportionation [Eq. (2)]. In contrast  $R_4Pb$  even with higher alkyl groups is still a good alkylating reagent. Thus the satisfactory preparation of dialkylgermanium dichloride is possible (R = butyl).



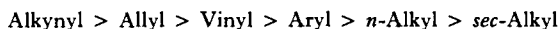
Further alkylation of the dichloride to  $R_3GeCl$  was unsuccessful, and even the more reactive tetraalkyllead did not show any reaction at 90° C.



The analogous alkylations with tetraalkyltin are much slower because of the higher dissociation energy of the C—Sn bond (189). Thus one has to work with tetrabutyltin at 210° C and in an autoclave (173). The kinetics of cleavage of aliphatic and aromatic carbon–lead bonds has been studied several times in past years (29, 46, 47, 56, 57, 75, 110, 115, 173, 178, 237).

### B. Lead Tetraalkyls with Different Organic Groups

Starting materials are mostly symmetrical lead tetraalkyl compounds. One or two of the alkyl groups are cleaved by suitable reagents, and different alkyl groups are attached. For the synthesis of  $R_4Pb$  compounds with three or four *different* substituents, consideration of the following order of decreasing reactivity of the Pb—C bond towards polar reagents is crucially important (partly after 91, 150):



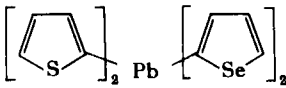
In order to detect small differences in reactivity the reaction conditions and reaction mechanism must be the same for all examples. If this is not the case, the results are contradictory (compare Neumann, 189).

Lead alkyl compounds with four different ligands on the lead atom have been known for a long time (149). Although attempts were made by Krause in 1917 and 1925 (150), separation of optical isomers has never been accomplished. Table II lists the organolead compounds without functional groups prepared since 1963.

### C. Lead Tetraalkyls with Functional Groups on a Carbon Atom

Until lately, with very few exceptions the only lead alkyls known were those which had simple alkyl or aryl groups on the metal atom or their

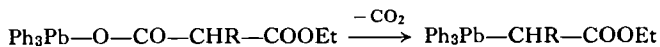
TABLE II  
LEAD TETRAALKYLS WITHOUT FUNCTIONAL GROUPS PREPARED SINCE 1963

Compounds	Properties	References
$(C_6F_5)_4Pb$	M.p. 199°–200° C, subl.; 40° C in vacuum	62, 108, 266, 267
$Ph_3PbC_6F_5$	M.p. 85°–87° C	62, 267
$Me_3PbC_6F_5$	B.p. 40°–45° C/0.01 mm	62
$(C_5H_5)_2Pb(C_6F_5)_2$	—	266
	M.p. 147° C	280
$(n-C_{16}H_{33})_4Pb$	M.p. 40.5°–41° C	210
$(C_5H_5)_2PbMe_2$	Yellow crystals; unstable, decomposes 0° C, gives $Pb(C_5H_5)_2$	66, 67
$(C_5H_5)_2PbEt_2$	Yellow crystals; unstable, decomposes 0° C, gives $Pb(C_5H_5)_2$	66
$(C_5H_5)PbMe_3$	Yellow crystals; stable in solution at 20° C;	66, 67
$(C_5H_5)PbEt_3$	Yellow crystals; stable in solution at 20° C	66, 67
$(C_5H_4Me)_2PbMe_2$	Deep yellow oil, yellow crystals; very unstable; decomposes at –15° C	66
$(C_5H_4Me)_2PbEt_2$	Deep yellow oil, yellow crystals; very unstable, stable at –20° C only for a few hours	66
$(C_5H_4Me)PbMe_3$	Yellow crystals; stable in solution at 20° C	66
$(C_5H_4Me)PbEt_3$	Deep yellow oil; decomposes above 0° C	66
$(Ph_3Pb)_4C$	Decomp. 292°–294° C	277
$(Ph_3Pb)_3CH$	M.p. 167°–169° C; 166° C	277
$(Ph_3Pb)_2CH_2$	M.p. 94°–95° C; 97° C	277
$(Ph-CMe_2-CH_2)_4Pb$	M.p. 88°–89° C	285

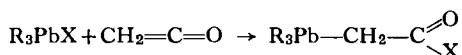
partially substituted derivatives in which halogen, hydroxyl, alkoxyl, or acyloxy replaced one or more of the organic groups. Organolead compounds with alkyl and aryl ligands containing functional groups are of interest for further reactions. The methods used in organic chemistry to introduce functional groups into organic molecules such as nitration, halogenation, and sulfonation are too strenuous to apply directly to organolead compounds because the lead–carbon bonds are cleaved under these conditions. For the synthesis of functionally substituted lead tetraalkyls and tetraaryls, procedures are used in which the functional group is introduced together

with the organic substituent. A limitation to this method is that it is not possible to prepare functionally substituted Grignard compounds with  $\text{NO}_2$ ,  $\text{SO}_3\text{H}$ ,  $\text{CN}$ , or carbonyl groups.

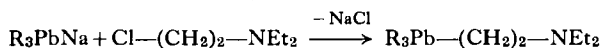
Kozeschkow and Alexandrow (146) obtained  $\alpha$ -plumbylcarboxylic acid esters starting from plumbyl half-esters of malonic acid which decarboxylate at  $180^\circ\text{C}$ .



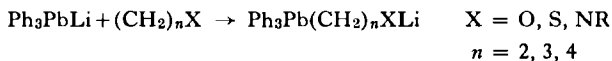
The reaction is limited to compounds which decarboxylate below  $180^\circ\text{C}$  because otherwise a decomposition of the organolead compounds takes place, especially because of the greater instability of compounds with an electronegative group in the position  $\alpha$  to the  $\text{Pb}-\text{C}$  bond. The preparation of  $\alpha$ -substituted compounds by addition of  $\text{Ph}_3\text{PbX}$  to ketenes was investigated by Willemsens and van der Kerk (276) and succeeds only if  $\text{X}$  is  $\text{OH}$  or  $\text{CH}_3\text{COO}$ .



Gilman *et al.* (83, 87, 262) obtained some lead tetraalkyls substituted with hydroxy and tertiary amino groups.



The procedure is of no use if the substituents react with the lead-sodium compound or if an alkali metal-halogen exchange takes place. Unfortunately this happens in most cases, i.e., for nitriles, esters, unsubstituted amines, carboxylic acids, alcohols, unsaturated compounds, etc. Thus the reaction of ethyl  $\alpha$ -bromoacetate with  $\text{Ph}_3\text{PbLi}$  does not give the expected plumbyl derivative, but gives mainly  $\text{Ph}_3\text{PbBr}$  and  $\text{Ph}_6\text{Pb}_2$ . The reaction with methyl  $\beta$ -chloropropionate gives, after hydrolysis,  $\text{PbO}$  along with the corresponding acrylic ester and benzene (274). Recently Willemsens and van der Kerk (275) succeeded in the synthesis of several functionally substituted organolead compounds by a reaction of  $\text{R}_3\text{MLi}$  compounds with heterocyclic compounds originally found by Gilman (92).



In some cases the synthesis of bromine-substituted organolead compounds from  $\text{Ph}_3\text{PbLi}$  and an excess of  $\alpha,\omega$ -dibromoalkanes (95) is successful (see Table III). These bromides form azides with sodium azide, which themselves react with alkynes (118) to give triazoles by 1,3-addition.

TABLE III  
LEAD TETRAALKYLS WITH FUNCTIONAL GROUPS AT THE CARBON ATOMS

Compound	Procedure for preparation	References
$\text{Ph}_3\text{PbCH}_2\text{COOEt}$	Decarboxylation of $\text{Ph}_3\text{PbOCO}-\text{CH}_2-\text{COOEt}$	146, 274
$\text{Ph}_3\text{PbCH}(\text{C}_6\text{H}_5\text{CH}_2)\text{COOEt}$	Decarboxylation of $\text{Ph}_3\text{PbOCO}-\text{CHR}-\text{COOEt}$	146, 274
$\text{Ph}_3\text{PbCH}_2\text{CN}$	Decarboxylation of $\text{Ph}_3\text{PbOCO}-\text{CH}_2-\text{CN}$	274
$(\text{Ph}_3\text{PbCH}_2\text{CO})_2\text{O}$	$2 \text{ Ph}_3\text{PbOH} + 4 \text{ CH}_2=\text{C}=\text{O} - \text{Ac}_2\text{O}$	274, 276
$\text{Ph}_3\text{PbCH}_2\text{COOEt}$	$\text{Ph}_3\text{PbOCOCH}_3 + \text{CH}_2=\text{C}=\text{O} + \text{EtOH} - \text{HOAc}$	274, 276
$\text{Ph}_3\text{PbCH}_2\text{CH}_2\text{CH}_2\text{NEt}_2$	$\text{Ph}_3\text{PbLi} + \text{ClCH}_2\text{CH}_2\text{CH}_2\text{NEt}_2$	87, 262
$\text{Et}_3\text{PbCH}_2\text{CH}_2\text{NEt}_2$	$\text{Et}_3\text{PbNa} + \text{Cl}(\text{CH}_2)_n\text{NEt}_2$	83
$\text{Et}_3\text{PbCH}_2\text{CH}_2\text{CH}_2\text{NEt}_2$	$\text{Et}_3\text{PbNa} + \text{Cl}(\text{CH}_2)_n\text{NEt}_2$	83
$\text{Ph}_3\text{PbCH}_2\text{CH}_2\text{OH}$	$\text{Ph}_3\text{PbLi} + \left\{ \begin{array}{l} \text{epoxide} \\ \text{thiolane} \\ \text{N-methylcarbamate} \\ \text{N-phenylcarbamate} \\ \text{chloromethyl epoxide} \\ \text{oxetane} \\ \text{oxetanone} \end{array} \right.$	274, 275
$\text{Ph}_3\text{PbCH}_2\text{CH}_2\text{SH}$		274, 275
$\text{Ph}_3\text{PbCH}_2\text{CH}_2\text{NHCOMe}$		274, 275
$\text{Ph}_3\text{PbCH}_2\text{CH}_2\text{NHCOPh}$		274, 275
$\text{Ph}_3\text{PbCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$		274, 275
$\text{Ph}_3\text{PbCH}_2\text{CH}_2\text{CH}_2\text{OH}$		274, 275
$\text{Ph}_3\text{PbCH}_2\text{CH}_2\text{COOMe}$		274, 275


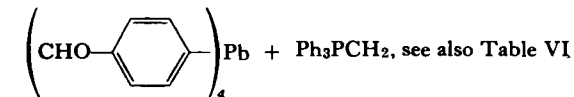
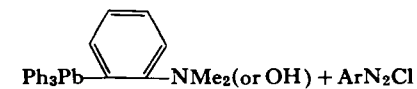
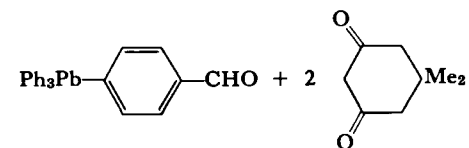
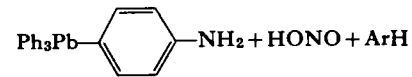
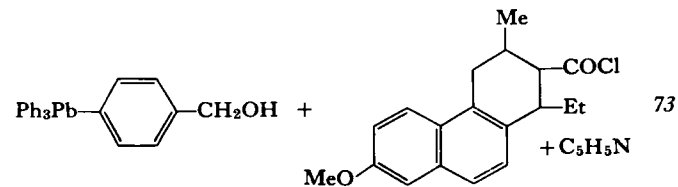
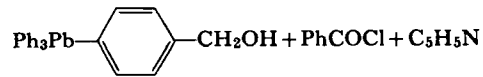
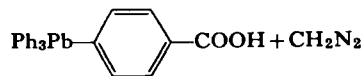
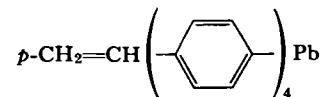
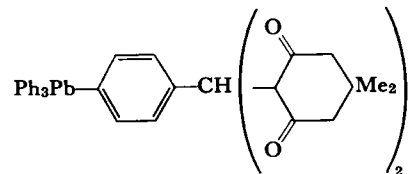
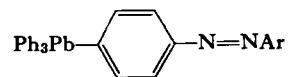
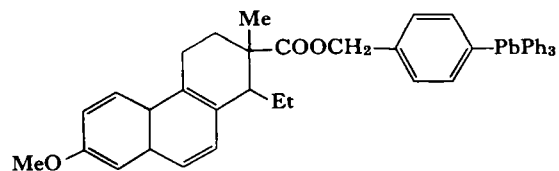
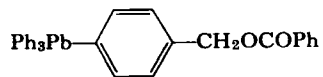
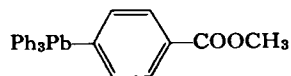
Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>3</sub> Br	Ph <sub>3</sub> PbLi + $\begin{cases} \text{Br(CH}_2)_3\text{Br} \\ \text{Br(CH}_2)_4\text{Br} \\ \text{Br(CH}_2)_5\text{Br} \end{cases}$	95
Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>4</sub> Br		95
Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>5</sub> Br		95
Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>3</sub> N <sub>3</sub>	Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>3</sub> Br + NaN <sub>3</sub>	95
Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>4</sub> N <sub>3</sub>	Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>4</sub> Br + NaN <sub>3</sub>	95
Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>5</sub> N <sub>3</sub>	Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>5</sub> Br + NaN <sub>3</sub>	95
Ph <sub>3</sub> Pb $\begin{array}{c} \text{HC}=\text{C}-\text{C(OH)(CH}_3)_2 \\   \quad   \quad   \\ (\text{CH}_2)_n-\text{N}-\text{N}=\text{N} \end{array}$	Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>3</sub> N <sub>3</sub>	95
$n = 3, 4, 5$	Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>4</sub> N <sub>3</sub> + (CH <sub>3</sub> ) <sub>2</sub> C(OH)C≡CH	95
Me <sub>3</sub> PbCF <sub>3</sub>	Ph <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>5</sub> N <sub>3</sub>	95
Me <sub>3</sub> PbC <sub>2</sub> F <sub>5</sub>		
	Me <sub>4</sub> Pb + CF <sub>3</sub> I	130
	Me <sub>4</sub> Pb + C <sub>2</sub> F <sub>5</sub> I + UV	130
	Me <sub>6</sub> Pb <sub>2</sub> + C <sub>2</sub> F <sub>5</sub> I	130
Ph <sub>3</sub> PbCCl <sub>3</sub>	Ph <sub>3</sub> PbOMe + O=C(CX <sub>3</sub> ) <sub>2</sub> — CX <sub>3</sub> —C(=O)OCH <sub>3</sub>	42-44
Ph <sub>3</sub> PbCBr <sub>3</sub>	X = Cl, Br	42-44
Ph <sub>3</sub> PbCHCl <sub>2</sub>	Ph <sub>3</sub> PbLi + HCCl <sub>3</sub>	274
(Ph <sub>3</sub> Pb) <sub>2</sub> CCl <sub>2</sub>	2 Ph <sub>3</sub> PbLi + CCl <sub>4</sub>	274
Et <sub>3</sub> PbCH <sub>2</sub> Cl	Et <sub>3</sub> PbCl + CH <sub>2</sub> N <sub>2</sub>	278, 279
Et <sub>3</sub> PbCHClCH <sub>3</sub>	Et <sub>3</sub> PbCl + CH <sub>3</sub> —CHN <sub>2</sub>	278, 279
Et <sub>2</sub> Pb(CH <sub>2</sub> Cl) <sub>2</sub>	Et <sub>2</sub> PbCl <sub>2</sub> + 2 CH <sub>2</sub> N <sub>2</sub>	279
Et <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>5</sub> Br	Et <sub>2</sub> Pb  + Br <sub>2</sub> + EtMgBr	96
Me <sub>3</sub> Pb(CH <sub>2</sub> ) <sub>5</sub> SnMe <sub>3</sub>	Me <sub>3</sub> PbBr + BrMg(CH <sub>2</sub> ) <sub>5</sub> SnMe <sub>3</sub>	98

TABLE III—continued

Compound	Procedure for preparation	References
$(\text{Me}_3\text{SiCH}_2)_4\text{Pb}$	$\text{PbCl}_2 + \text{ClMgCH}_2\text{SiMe}_3$	249
$\text{Me}_3\text{PbCH}_2\text{SiMe}_3$	$\text{Me}_3\text{PbCl} + \text{ClMgCH}_2\text{SiMe}_3$	244
$\text{Ph}_3\text{PbCH}_2\text{PbPh}_3$	$2 \text{ Ph}_3\text{PbLi} + \text{CH}_2\text{Br}_2$	95
$\text{Ph}_3\text{Pb}(\text{CH}_2)_2\text{PbPh}_3$	$2 \text{ Ph}_3\text{PbLi} + \text{BrCH}_2\text{CH}_2\text{Br}$	87
$\text{Ph}_3\text{Pb}(\text{CH}_2)_4\text{PbPh}_3$	$2 \text{ Ph}_3\text{PbLi} + \text{Br}(\text{CH}_2)_4\text{Cl}$	262
$\text{Pb}(\text{CH}_2\text{CH}_2\text{CN})_4$	Electrolyses of $\beta$ -iodopropionitrile on a Pb cathode	268
$\text{Ph}_3\text{PbCH}_2\text{COOH}$	Hydrolysis of $\text{Ph}_3\text{PbCH}_2\text{—COOEt}$	161
$\text{Ph}_3\text{PbC}_6\text{H}_4\text{CH}_2\text{OH}$	$\text{Ph}_3\text{PbCl} + \text{Li—C}_6\text{H}_4\text{—CH}_2\text{OLi}$ , Hydrol.	83
$\text{Ph}_3\text{PbCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$	$\text{Ph}_3\text{PbAlI} + \text{KMnO}_4$	15
$\text{Ph}_3\text{Pb—C}_6\text{H}_4\text{—COOH}$	$\text{Ph}_3\text{Pb—C}_6\text{H}_4\text{—CH}_2\text{OH} + \text{KMnO}_4$	83
$\text{Ph}_3\text{Pb—C}_6\text{H}_4\text{—CHO}$	$\text{Ph}_3\text{Pb—C}_6\text{H}_4\text{—CH}_2\text{OH} + \text{MnO}_2$	73
$\text{Me}_3\text{Pb—C}_6\text{H}_4\text{—CH}_2\text{CH}_2\text{SnPh}_3$	$\text{Me}_3\text{Pb—C}_6\text{H}_4\text{—CH=CH}_2 + \text{Ph}_3\text{SnH}$	209
$\left( \text{Me}_3\text{Pb—C}_6\text{H}_4\text{—CH}_2\text{CH}_2 \right)_2 \text{SnPh}_2$	$2 \text{ Me}_3\text{Pb—C}_6\text{H}_4\text{—CH=CH}_2 + \text{Ph}_2\text{SnH}_2$	209
$\text{R}_3\text{Pb—C}_6\text{H}_4\text{—N}^+\text{Me}_2\text{Me} \quad \text{I}^-$	$\text{R}_3\text{Pb—C}_6\text{H}_4\text{—NMe}_2 + \text{MeI}$	57, 87, 262



81, 83

73

73

85

73

86

50

TABLE III—continued

Compound	Procedure for preparation	References
$\text{Ph}_3\text{Pb}-\text{C}_6\text{H}_4-\text{COOH}$	$\text{Ph}_3\text{Pb}-\text{C}_6\text{H}_4-\text{Br} + \text{Et}_2\text{Ba} + \text{CO}_2$	81
$\text{Pb}\left(\text{C}_6\text{H}_4-\text{CHO}\right)_4$	$\text{BrMg}-\text{C}_6\text{H}_4-\text{C}\begin{matrix} \text{O} \\ \diagup \\ \text{O} \end{matrix} + \text{PbCl}_4$	50
$[\text{PbEt}_4(\text{NO})_2]^{2+}[\text{NO}_3]_2^{2-}$	$\text{R}_4\text{Pb} + 2 \text{N}_2\text{O}_4$	107
$[\text{PbProp}_4(\text{NO})_2]^{2+}[\text{NO}_3]_2^{2-}$	$\text{R}_4\text{Pb} + 2 \text{N}_2\text{O}_4$	107



Some special procedures which are not discussed are mentioned in Table III. Also of interest are those reactions of functionally substituted organolead compounds, in which the functional groups are exchanged without cleavage of the lead-carbon bond (see Table III).

Not tabulated are compounds which have functional groups on a phenyl substituent, i.e.,  $\text{CF}_3$  (94), halogen (57, 83), ether (57, 78, 82, 83, 86, 90, 150), amine (16, 57, 61, 85, 86, 88, 94, 262), sulfonamide (61), and  $\text{Me}_3\text{Si}$  (97) and which are accessible via the Li or Mg organic compounds. Also, unsaturated lead alkyls, e.g., allyl, vinyl, or alkynyl groups, are not mentioned here, because they are treated separately in Section II,D.

As mentioned above, many surprising syntheses are possible with the help of compounds containing  $\text{Pb-H}$ ,  $\text{Pb-N}$ , and  $\text{Pb-O}$  groups. Substances so prepared will not be discussed here but are considered in connection with the individual syntheses; see Sections III,B-D, IV,B,C, and V,B. It has become possible to introduce plumbyl groups under very mild conditions as substituents into complicated organic compounds, by using the appropriate lead alkyls as specific reagents.

#### D. Unsaturated Lead Tetraalkyls

In the past few years unsaturated organolead compounds have become of special interest. They are starting materials for lead-containing polymers (125) (see Sections 2 and 4 below), and the unsaturation makes the  $\text{Pb-C}$  bond especially reactive. For their preparation the procedures described in Sections II,B,C are mainly of interest.

##### 1. Allyl Compounds

Allyllead compounds are the most unstable thermally of all  $\text{Pb-C}$  compounds. Only compounds with *one* allyl group directly bound to lead are known with certainty (see Table IV). Experiments to isolate  $\text{Ph}_2\text{PbAll}_2$  were unsuccessful (80, 105). If the allyl group is separated from the lead atom by an inserted phenyl ring the stability is increased (see Table VI), as can be seen by the following reaction (224) (compare Section D,4):

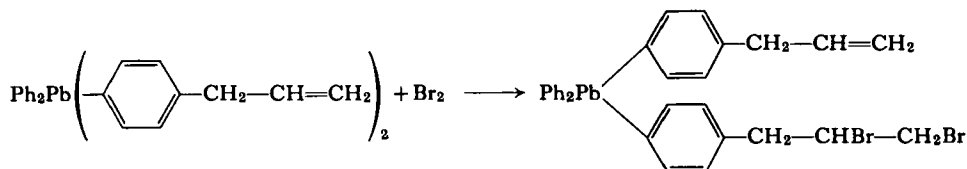
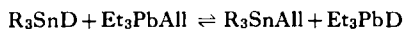
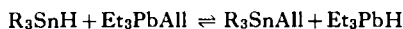


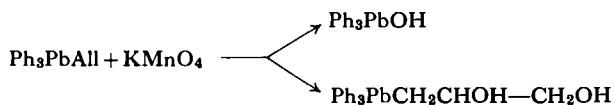
TABLE IV  
LEAD TETRAALKYLS WITH ALLYL GROUPS ON LEAD

Compound	Procedure	Properties	References
$(\text{CH}_2=\text{CHCH}_2)_4\text{Pb}$	$\text{CH}_2=\text{CHCH}_2\text{MgBr} + \text{PbCl}_2$	Not identified, results uncertain	270
$(\text{CH}_2=\text{CHCH}_2)_2\text{PbPh}_2$	$\text{CH}_2=\text{CHCH}_2\text{MgBr} + \text{Ph}_2\text{PbCl}_2$	Decomposes; cannot be isolated in pure form	80, 105
$(\text{CH}_2=\text{CHCH}_2)\text{PbPh}_3$	$\text{CH}_2=\text{CHCH}_2\text{MgBr} + \text{Ph}_3\text{PbCl}$	M.p. $76^\circ\text{--}77^\circ\text{C}$	15, 80, 145
$(\text{CH}_2=\text{CHCH}_2)\text{PbEt}_3$	$\text{CH}_2=\text{CHCH}_2\text{—X} + \text{R}_3\text{Pb—alkali}$	B.p. $86^\circ\text{C}/10\text{ mm}$ ; $n_D^{20}$ 1.5423; $d_{23}$ 1.6056	161
$(\text{CH}_2=\text{CMe—CH}_2)\text{PbEt}_3$	$\text{CH}_2=\text{C—CH}_2\text{Cl} + \text{Et}_4\text{Pb}$   $\text{CH}_3$	B.p. $45^\circ\text{--}50^\circ\text{C}/10^{-1}\text{ mm}$ ; colorless liquid	94

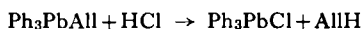
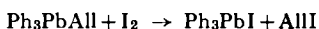
The allyl group is easily cleaved from the lead by organotin hydrides. At room temperature the following equilibrium is reached in a short time (see Section III,A,1,e) (153):



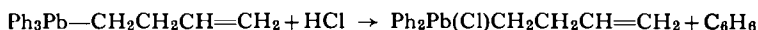
Triphenyltin hydride and allyl triphenyllead do not exchange ligands at 20° C, but at 70° C Pb precipitates and  $Ph_6Sn_2$  is formed (105). Oxidation of  $Ph_3PbAlI$  with  $KMnO_4$  in acetone gives two products (15).



Iodine or alcoholic HCl cleaves the compound at 20° C in the following way (145):



On the other hand triphenyl-3-butenyllead reacts with HCl in the same way as a saturated lead alkyl (91).



## 2. Vinyl Compounds

The vinyl compounds are thermally more stable than the allyl derivatives. For a critical review up to 1959 see Kaesz and Stone (131). Several investigators are engaged in the synthesis and reactions of the vinyllead compounds (Table V). Tetravinyllead, first synthesized in 1959, can be distilled under vacuum and is colorless but less stable than tetraethyllead. The vinyllead grouping is more easily cleaved than the  $Pb-C$  bond in saturated organolead compounds.

Alkali metals (114, 129), lithium alkyls (60, 129, 251), silver nitrate (112, 113), halogens, acids (112, 128), and metal and nonmetal halides (20, 21, 113, 176) are capable of cleaving the vinyl group under very mild conditions; thus the otherwise difficult syntheses of vinyl lithium and vinyl silver are made possible.

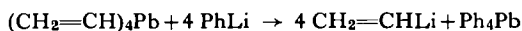
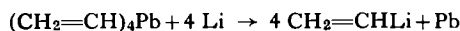
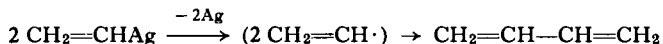


TABLE V  
LEAD TETRAALKYLS WITH VINYL GROUPS ON THE LEAD

Compound	Procedure for preparation	Properties	References
$\text{Vi}_4\text{Pb}$	$\text{ViMgBr} + \text{PbCl}_4, \text{PbCl}_2, (\text{NH}_4)_2\text{PbCl}_6$	B.p. $69^\circ\text{--}70^\circ\text{C}/11\text{ mm}$ ; $n_D^{20}$ 1.5462; $d_4^{20}$ 1.7882	20, 21, 128, 176, 229
$(\text{CF}_2=\text{CF})_4\text{Pb}$	$\text{CF}_2=\text{CFMgBr} + \text{PbCl}_4, (\text{NH}_4)_2\text{PbCl}_6$	B.p. $51^\circ\text{--}52^\circ\text{C}/8\text{ mm}$ ; $n_D^{18}$ 1.4193; $d_{18}$ 2.4020; $d_{23}$ 2.4020	227
$(\text{CH}_2=\text{CH})_3\text{PbEt}$	$\text{CH}_2=\text{CHMgBr} + \text{EtPbCl}_3$	—	20
$(\text{CH}_2=\text{CH})_3\text{PbPh}$	$\text{CH}_2=\text{CHMgBr} + \text{PhPbCl}_3$	—	20
$(\text{CH}_2=\text{CH})_2\text{PbEt}_2$	$\text{CH}_2=\text{CHMgBr} + \text{Et}_2\text{PbCl}_2$	B.p. $30^\circ\text{C}/1\text{ mm}$	20, 141
$(\text{CH}_2=\text{CH})_2\text{PbPh}_2$	$\text{CH}_2=\text{CHMgBr} + \text{Ph}_2\text{PbCl}_2$	B.p. $120^\circ\text{--}155^\circ\text{C}/0.05\text{ mm}$ B.p. $111^\circ\text{--}114^\circ\text{C}/0.002\text{ mm}$	111, 128
$(\text{CH}_2=\text{CH})\text{PbEt}_3$	$\text{CH}_2=\text{CHMgBr} + \text{Et}_3\text{PbCl}$	—	20, 141
$(\text{Me}_2\text{C}=\text{CH})\text{PbEt}_3$	$\text{Me}_2\text{C}=\text{CHLi} + \text{Et}_3\text{PbCl}$	B.p. $99^\circ\text{--}101^\circ\text{C}/12\text{ mm}$	93, 94
$(\text{PhCH}=\text{CH})\text{PbEt}_3$	$\text{Ph}-\text{CH}=\text{CHBr} + \text{Et}_4\text{Pb}$	B.p. $94^\circ\text{C}/10^{-2}\text{ mm}$ ; viscous, yellow liquid	94
$(\text{CH}_2=\text{CH})\text{PbPh}_3$	$\text{CH}_2=\text{CHMgBr} + \text{Ph}_3\text{PbCl}$ (Cl) (Br)	B.p. $160^\circ\text{--}170^\circ\text{C}/0.05\text{ mm}$ ; m.p. $33^\circ\text{--}34^\circ\text{C}$	105, 128, 251

Vinylsilver decomposes around  $-30^{\circ}\text{C}$ , mainly to Ag and butadiene.



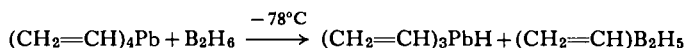
Vinyl substituents on lead are cleaved by sodium in liquid ammonia (111) with greater difficulty than alkyl substituents. Tetravinyllead can also be used as an alkenylating agent in the same way as the tetraorganolead compounds. Thus boron trichloride at  $-78^{\circ}\text{C}$  with  $\text{Vi}_4\text{Pb}$  yields, almost quantitatively, trivinylboron (113).



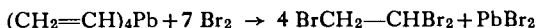
MX compounds where  $\text{M}=\text{P}$ , As, Sb and  $\text{X}=\text{Cl}$ , Br are transformed upon heating for 20–25 hours into the mono- and divinyl halogen compounds (176) (compare Bartocha *et al.*, 20) such as those with  $\text{M}=\text{Al}$ , Si, P (21), e.g.,



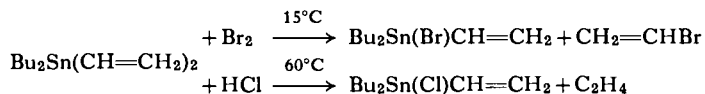
The reactivity of the vinyllead bond is clearly shown in the reaction of  $\text{Vi}_4\text{Pb}$  with diborane (113). Even at  $-78^{\circ}\text{C}$  one hydrogen atom is quantitatively exchanged, while with  $\text{Me}_4\text{Pb}$  at higher temperatures no reaction takes place (see Section III, A, 1, e).



Halogen cleaves from two to four vinyl substituents at  $20^{\circ}\text{C}$  (112, 128). Degradation with bromine gives  $\text{PbBr}_2$  and 1,1,2-tribromoethane.



In the presence of excess  $\text{Vi}_4\text{Pb}$ , vinyl bromide is also formed, proving that the  $\text{Pb}-\text{C}$  bond is cleaved before bromination of the  $\text{C}=\text{C}$  double bond takes place. Hydrochloric acid in the presence of a twofold excess of  $\text{Vi}_4\text{Pb}$  cleaves only one vinyl substituent at  $-78^{\circ}\text{C}$ ; with saturated lead tetraalkyl compounds this reaction takes place only at much higher temperatures. A comparison of the reactivities with vinyltin compounds is interesting: bromine and hydrochloric acid cleave from dibutyldivinyltin not more than one vinyl substituent (238, 248).



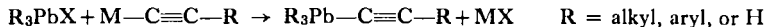
From tetrakis(perfluorovinyl)lead the trifluorovinyl substituents are cleaved even with bases such as trifluoroethylene (259). Vinyllead compounds are of technical interest as antiknocking agents (59, 133) and for the synthesis of lead-containing polymers. However, tetravinyllead gives only copolymers with styrene; in the same way mono- and divinyllead ethyls were copolymerized with peroxide catalysts at 120°–130° C with styrene and  $\alpha$ -methylstyrene (141).

### 3. Alkynyl Compounds

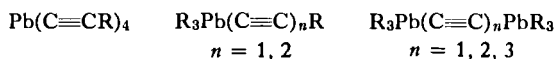
During the last 15 years much work has been done on plumbalkynes. After Gilman (36) reported in 1938 the reactions of sodium acetylides with triorganolead halides, this procedure was developed by several groups (99, 180, 269, 281).

A summary of all alkynyllead compounds prepared up to 1965 is given by Davidsohn and Henry (41); therefore, we will deal with them only briefly. Four procedures are known for the preparation of alkynylleads.

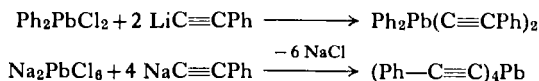
(1) The reaction of alkali acetylides or alkynyl Grignard compounds (124) with organolead halides in liquid  $\text{NH}_3$  or an organic solvent yields alkynyl-substituted lead compounds.



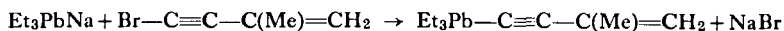
The following types of compounds have been obtained by this method:



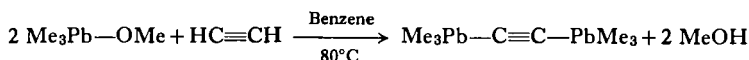
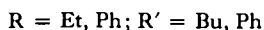
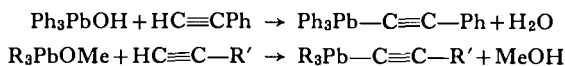
Alkynylleads with three alkyne substituents on the lead atom are still unknown. Apparently, the synthesis of di- and tetraalkynes has recently been successful (120).



(2) Reactions of organolead-alkali metal compounds with halogenated acetylenes have seldom been used until now (281).

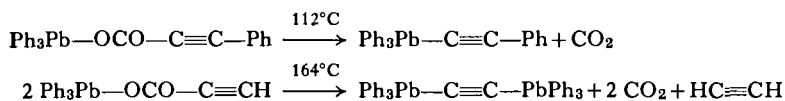


(3) The condensation used recently for the synthesis of alkynyltins from monosubstituted acetylenes with organotin amines, oxides, and halides (135, 160, 193, 253) has been shown by Davies and Puddephatt to be successful with organolead compounds (45).



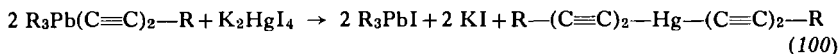
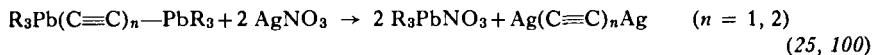
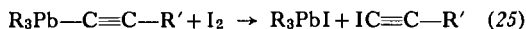
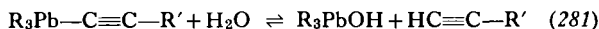
This procedure is very mild and should be the most suitable method to prepare alkynyllead compounds with functional groups such as CN, CONH<sub>2</sub>, =CO, etc. These still unknown compounds cannot be prepared by the first two procedures mentioned and would certainly be difficult to obtain by the fourth procedure.

(4) Triphenylplumbyl half-esters of malonic acid can be decarboxylated, as mentioned in Section C, with the formation of a new Pb—C bond. Willemsens and van der Kerk (274) and Davies *et al.* (45) have extended this procedure to other triphenylplumbyl esters of carboxylic acids, an example being phenylpropionic acid.

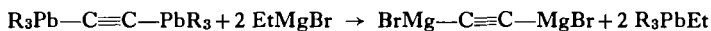


Of course this procedure is limited to compounds which decarboxylate easily; otherwise decomposition takes place.

In spite of the synthesis of numerous new alkynyllead compounds, knowledge about their reactivity is very limited. The Pb—C≡ bond is generally more susceptible to polar reagents such as water, halogen, K<sub>2</sub>HgI<sub>4</sub>, and AgNO<sub>3</sub> than the vinyllead grouping.



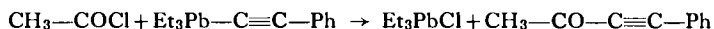
Copper(I) compounds cleave analogously (25). It has been reported that compounds such as R<sub>3</sub>Pb—(C≡C)—PbR<sub>3</sub> are not attacked by water or aqueous alkali (100). The following exchange takes place with Grignard compounds (25):



Monosubstituted products easily disproportionate to the disubstituted alkynylleads (25).

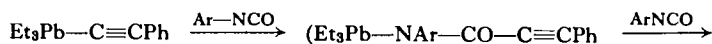


Davies and Puddephatt recently established (43, 45) that the alkynyllead grouping is cleaved easily in polar reactions, but less readily than alkynyl Grignard compounds. Thus mild syntheses are possible e.g., with acid chlorides.

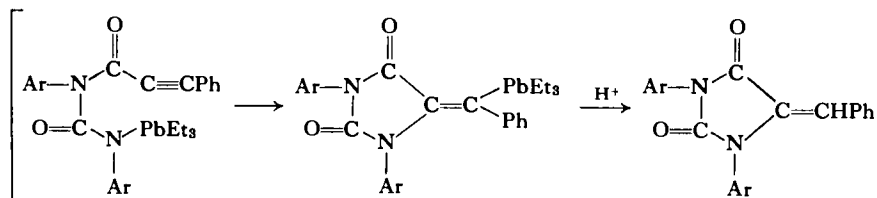


The yield of alkynyl ketone is high, about 84% to 96%. The corresponding Grignard compound gives yields of only 8–15%.

Phenyl- and 1-naphthylisocyanate react exothermically, to give compounds which were first thought to be uracil derivatives (43), but finally were identified as hydantoins. After hydrolysis of the vinyllead grouping the lead-free 1,3-diaryl-5-benzylidene hydantoin is formed. The following pathway is proposed and is well supported by different arguments (45):



Ar = Ph or 1-naphthyl



Again the smooth and specific reaction of alkynylleads has to be emphasized. The analogous stannic derivatives also give the hydantoin but only after 18 hours at 120° C (135, 192).  $\text{Ph}-\text{C}\equiv\text{C}-\text{MgBr}$  gives on the other hand the phenylpropiolylanilide,  $\text{PhNH}-\text{CO}-\text{C}\equiv\text{CPh}$ , with  $\text{PhNCO}$  while  $\text{Ph}-\text{C}\equiv\text{CNa}$  gives a complex reaction (26).

#### 4. Other Unsaturated Lead Tetraalkyls

Reactions of unsaturated substituents are made more likely if the substituents are not directly connected to the lead atom but are separated from it by a phenyl group. A large number of these compounds have recently become known (see Table VI).



TABLE VI  
LEAD TETRAALKYLS WITH ALLYL AND VINYL GROUPS ON CARBON ATOMS

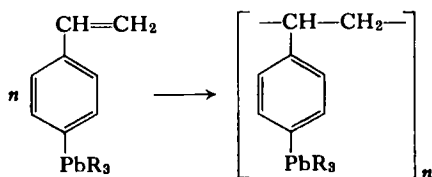
Compound	Procedure	Properties	References
$p\text{-H}_2\text{C}=\text{CHCH}_2\text{C}_6\text{H}_4\text{PbPh}_3$	$n\text{-}p\text{-H}_2\text{C}=\text{CHCH}_2\text{C}_6\text{H}_4\text{MgBr} +$	M.p. 206° C	224
$(p\text{-H}_2\text{C}=\text{CHCH}_2\text{C}_6\text{H}_4)_2\text{PbPh}_2$		M.p. 194°–96° C	224
$(p\text{-H}_2\text{C}=\text{CHCH}_2\text{C}_6\text{H}_4)_4\text{Pb}$	$\text{Ph}_{4-n}\text{PbCl}_n$	Polymerizes easily	225
$(p\text{-CH}_2=\text{CHC}_6\text{H}_4)_4\text{Pb}$	$(\text{C}_6\text{H}_4\text{-}p\text{-CH}=\text{CH}_2)\text{MgBr} + (\text{NH}_4)_2\text{PbCl}_6$ , see also Table III	Soluble in $\text{C}_6\text{H}_6$ , $\text{CH}_2\text{Cl}_2$ and $\text{CHCl}_3$ soluble	49
$(p\text{-CH}_2=\text{CHC}_6\text{H}_4)_2\text{PbPh}_2$	$p\text{-CH}_2=\text{CHC}_6\text{H}_4\text{MgCl} + \text{Ph}_{4-n}\text{MX}_n$	M.p. 96°–97° C	206
$(p\text{-CH}_2=\text{CHC}_6\text{H}_4)\text{PbMe}_3$	$p\text{-CH}_2=\text{CHC}_6\text{H}_4\text{MgCl} + \text{Me}_3\text{PbBr}$	B.p. 60°–61° C/ $1.5 \times 10^{-4}$ mm; $n_D^{20}$ 1.6070; $d_4^{20}$ 1.7278	207
$(p\text{-CH}_2=\text{CMe}-\text{C}_6\text{H}_4)\text{PbMe}_3$	$p\text{-MgClC}_6\text{H}_4-\text{CMe}=\text{CH}_2 + \text{Me}_3\text{PbBr}$	B.p. 69°–71° C/ $10^{-3}$ mm; $n_D^{20}$ 1.5963; $d_4^{20}$ 1.6816	207
$(p\text{-CH}_2=\text{CHC}_6\text{H}_4)\text{PbEt}_3$	$p\text{-CH}_2=\text{CHC}_6\text{H}_4\text{MgCl} + \text{Et}_3\text{PbCl}$	Polymerizes easily; stable at 20° C	218
$(p\text{-CH}_2=\text{CMe}-\text{C}_6\text{H}_4)\text{PbEt}_3$	$p\text{-CH}_2=\text{CMe}-\text{C}_6\text{H}_4\text{MgBr} + \text{PbEt}_3\text{Cl}$	B.p. 148°–149° C/3 mm; $n_D^{20}$ 1.5796; $d_{20}$ 1.527	142, 221
$(p\text{-CH}_2=\text{CHC}_6\text{H}_4)\text{PbPh}_3$	$p\text{-CH}_2=\text{CHC}_6\text{H}_4\text{MgCl} + \text{Ph}_3\text{PbCl}$	M.p. 107°–109° C	206, 218
2,4-Me(CH <sub>2</sub> =CH)C <sub>6</sub> H <sub>3</sub> PbPh <sub>3</sub>	—	M.p. 101°–105° C	<sup>a</sup>
2,4-(CH <sub>2</sub> =CH)(Me)C <sub>6</sub> H <sub>3</sub> PbPh <sub>3</sub>	—	M.p. 110°–112° C	

<sup>a</sup> Both compounds are mentioned in Dub (52) but not described in the literature.

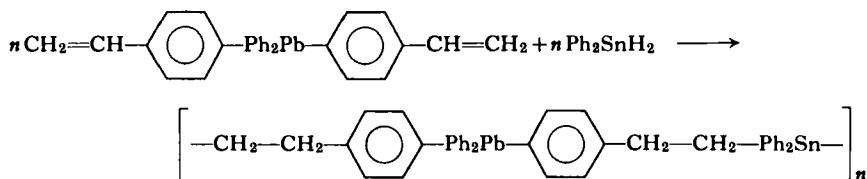
The *p*-allylphenyl grouping can be transformed to the dibromide without Pb—C cleavage (224).



*p*-Styrenyl derivatives of lead are polymerizable (142–144, 207, 218); the polymers contain lead in the side chains.



By addition of diphenyltin dihydride to diphenyldistyrenelead, polymers containing lead in the main chain were obtained (209).



This reaction is not transferable to the vinyllead and allyllead derivatives, because reductive elimination of the vinyl and allyl groups takes place (175). Numerous other lead alkenyls should be accessible in the same way as the lead alkyls. But only a few have been prepared, such as  $\text{Ph}_3\text{Pb}-\text{CH}_2\text{CH}_2-\text{CH}=\text{CH}_2$  already mentioned in Section II,D,1 (91).

### III

#### THE Pb—H BOND

##### A. Preparation and Reactivity of Organolead Hydrides

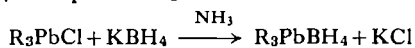
Many reactions have been carried out with the help of organic hydrides of the elements of the main group IV (except lead) which have resulted in the synthesis of new groups of compounds. Organotin hydrides were found to be especially versatile (189). The reactivity of organolead hydrides has presented a challenging problem that has only been recently solved. Some

physical characteristics of the Pb—H grouping have already been mentioned in Section I,B; see Table I.

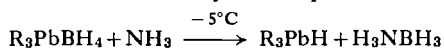
In the 1920's Paneth *et al.* (213) were able to isolate  $\text{SnH}_4$  (58, 216, 219). In spite of numerous experiments almost four decades elapsed before Holliday and Jeffers (109), while studying the reaction between  $\text{Me}_4\text{Pb}$  and  $\text{Al}(\text{BH}_4)_3$  in 1958, concluded from the reaction products  $\text{H}$ ,  $\text{Pb}$ ,  $\text{MeAl}(\text{BH}_4)_2$ , and methylleadborane that unstable methylleadboron hydrides exist. Considering that trimethyltin hydride had been prepared as early as 1922 by Kraus and Greer (148), the experimental difficulties which had to be overcome for the synthesis of organolead hydrides are evident. In the past the low stability of the Pb—H bond (see Table I) had not been sufficiently considered, and only a few useful reducing agents were available. It is therefore not surprising that no metal hydrides were used as reducing agents in one of the first experiments in the synthesis of organolead hydrides: Gilman and Bailie (78) reacted different  $\text{R}_3\text{PbNa}$  compounds with  $\text{NH}_4\text{Br}$  in liquid  $\text{NH}_3$ , but obtained  $\text{R}_6\text{Pb}_2$  instead of the expected hydrides. The corresponding reaction with  $\text{Ph}_3\text{PbNa}$  (65) also gave no hydride. Later Dickson and West (48) identified with the help of this method some  $\text{Et}_3\text{PbH}$ . The reductive cleavage of  $\text{Ph}_6\text{Pb}_2$  with  $\text{H}_2$  (also in the presence of catalysts) was tried only once, but without success (220). That this reaction could be suitable was shown in recent experiments by Gilman and Tomasi in silicon chemistry (89). They succeeded in cleaving the Si—Si bond with hydrogen in the presence of copper chromite catalyst. It is necessary that the Si—Si bond be activated by phenyl groups.

## 1. Syntheses

a. *With  $\text{KBH}_4$ .* Holliday and collaborators (53–55) succeeded in preparing  $\text{Me}_3\text{PbH}$  and  $\text{Et}_3\text{PbH}$  for the first time by reduction of the corresponding  $\text{R}_3\text{PbCl}$  with  $\text{KBH}_4$  in liquid  $\text{NH}_3$ .

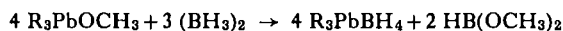


In the first step of the reaction trimethylleadboron hydride is formed and after evaporation of the liquid  $\text{NH}_3$  at  $-78^\circ\text{C}$  it remains as a solid colorless residue. Upon heating to  $-5^\circ\text{C}$  the complex decomposes to  $\text{Me}_3\text{PbH}$ , which can be isolated by short-path distillation at  $-196^\circ\text{C}$ .



b. *With  $\text{B}_2\text{H}_6$ .* The procedure recently discovered by Amberger and Hönigschmid-Grossich (11) is similar. Trialkyllead methoxides ( $\text{R} = \text{Me}$ ,

Et, *n*-propyl, *n*-bu) are reacted at  $-78^{\circ}\text{C}$  with diborane to give trialkylleads which are only slightly soluble in diethyl ether.



If one reacts the boronates at  $-78^{\circ}\text{C}$  with methanol, the trialkyllead hydrides are separated as colorless oils, hydrogen is evolved, and some Pb is formed.

c. *With LiAlH<sub>4</sub>*. With the aid of a LiAlH<sub>4</sub> procedure developed by Schlesinger *et al.* (63), Amberger (9) and also Becker and Cook (24) reported simultaneously in 1960 the reduction of methyl- and ethyllead halides to the hydrides in dimethyl ether.

Most of the other procedures for preparing lead hydrides give only small amounts of impure products. It is very probable that lead hydrides are catalytically decomposed by liquid NH<sub>3</sub>, which is often used as solvent. (The decomposition of tin hydrides is also catalyzed by NH<sub>3</sub> and amines.) The LiAlH<sub>4</sub> procedure appears to be the easiest and most successful for synthesis of large quantities of organolead compounds. To find the best conditions we reduced different organolead halides with LiAlH<sub>4</sub>, varying halogens, alkyl groups, and solvent (12, 188, 194). For the preparation of monohydrides we usually started with quite pure monochlorides which are readily accessible by reaction of the tetraalkyls with hydrochloric acid in hexane. The corresponding bromides can also be used but offer no advantage. The methyl- and ethyllead hydrides decompose below  $0^{\circ}\text{C}$ . Experience with organotin hydrides (189) indicated that larger alkyl groups should stabilize the molecules. Therefore, we also used tripropyl-, tri-*n*-butyl-, and isobutyllead chloride. The solvent and the amount of the reducing agent are of great importance in determining the course of the reduction.

(1) In diethyl ether some side reactions take place because the AlCl<sub>3</sub> formed during the course of the reaction apparently is not completely bound and therefore catalyzes decomposition of the hydride. Side reactions are suppressed by the use of more complexing ethers, THF, or diglyme, and the reaction takes place without precipitation of lead and evolution of gas. In the case of diglyme isolation of the hydride is almost impossible because of the high boiling point ( $160^{\circ}\text{C}$ ).

It was shown that a mixture of THF or (even better) diglyme and diethyl ether make the work-up much easier, because after hydrolysis with Seignette salt solution it is possible to separate the organic from the aqueous phase smoothly and to remove the relatively small amount of higher boiling ether.

(2) We observed that complete reduction is almost reached with a mole ratio of  $\text{LiAlH}_4:\text{R}_3\text{PbCl}$  of 1:2. With less  $\text{LiAlH}_4$  the products still contain some halogen, while with more, decomposition and  $\text{H}_2$  evolution takes place. In all experiments the chloride was dropped onto the reducing agent and it was found to be advantageous (mainly in experiments with more than 0.01 mole) to place first only one-half to one-third of the necessary  $\text{LiAlH}_4$  into the reaction vessel and to add, after the addition of all chloride, the rest of the reducing agent.

(3) Because organolead compounds are sensitive to light we kept all flasks in which the reduction was performed and in which the ether was evaporated ( $-10^\circ$  to  $0^\circ\text{C}$  and 1 torr) in small black cardboard boxes equipped with a cover. In this simple manner photolytic decomposition was avoided. Because of the thermal lability of the lead hydrides the reduction and hydrolysis have to take place at  $-60^\circ$  to  $-20^\circ\text{C}$ . Furthermore, the flasks and sintered glass funnels in which the hydride is placed after hydrolyzing  $\text{LiAlH}_4$  and drying over  $\text{MgSO}_4$  have to be precooled to  $-20^\circ$  to  $-40^\circ\text{C}$ . Absolutely clean flasks (cleaned with chromic acid) and exclusion of air are necessary. Using argon as a protecting gas, it was

TABLE VII  
ORGANOLEAD HYDRIDES

Compound	Procedure <sup>a</sup>	Purity <sup>b</sup>	Pb—H ( $\text{cm}^{-1}$ )	References
$\text{Me}_3\text{PbH}$	A, B, C	Not mentioned	1709	9, 24, 53–55
$\text{Me}_2\text{PbH}_2$	C	Not mentioned	—	9, 24
$\text{Et}_3\text{PbH}$	(A, B) C	95	1689	12, 24, 39, 188, 194
$\text{Et}_2\text{PbH}_2$	C	Not mentioned	1689	11
$\text{Vi}_3\text{PbH}$	E	Not mentioned	—	113
$\text{Pr}_3\text{PbH}$	(B) C	93	1675	11, 12, 188, 194
$\text{Bu}_3\text{PbH}$	(B) C	96	1680	11, 12, 188, 194
—, in equilibrium	D	—	1680	39, 198
$\text{Bu}_2\text{PbH}_2$	C	About 90 (in solution)	1640	12, 188, 194
iso- $\text{Bu}_3\text{PbH}$	C	75	1675	12, 188, 194
Cyclohex $_3\text{PbH}$	C	About 90 (in solution)	1650	12, 188, 194

<sup>a</sup> Methods: A,  $\text{R}_3\text{PbCl} + \text{KBH}_4$  (Section III,A,1,a); B,  $\text{R}_3\text{PbOMe} + \text{B}_2\text{H}_6$  (Section III, A,1,b); C,  $\text{R}_3\text{PbX} + \text{LiAlH}_4$ ;  $\text{R}_2\text{PbX}_2 + \text{LiAlH}_4$  (Section III,A,1,c); D,  $\text{R}_3\text{PbX} + \text{R}_3'\text{PbH}$  (Section III,A,1,e); E,  $\text{Vi}_4\text{Pb} + \text{B}_2\text{H}_6$  ( $-78^\circ\text{C}$ ).

<sup>b</sup> A simple and accurate criterion for purity; see Section III,B,1.

possible to prepare a number of organolead compounds on a 20–30 gm scale in a fairly pure state (12, 188, 194) (see Table VII). The preparation of tricyclohexyllead hydride is not yet satisfactory. The corresponding halides are not soluble in ethers such as THF or diglyme, and therefore some side reactions take place during the reduction. Hydrides with secondary substituents on lead apparently are less stable than those with primary substituents (compare also under halides).

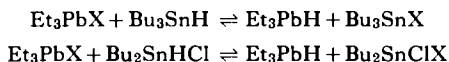
d. *With Organoaluminum Hydrides.* Dialkylaluminum hydrides are known to be excellent for the reduction of tin halides (123, 187, 200). It is astonishing that they have not yet been used for the preparation of organolead hydrides. They have two advantages over  $\text{LiAlH}_4$ : Reduction takes place in a homogeneous phase and side reactions are excluded in most cases. Furthermore the requirement for only a small amount of solvent (half as much as for the  $\text{LiAlH}_4$  procedure) simplifies the work-up.

$\text{Et}_2\text{AlH}$  and  $\text{iso-Bu}_2\text{AlH}$  reduce butyllead halides instantaneously at  $-60^\circ\text{C}$ . It is possible to follow the reduction spectroscopically; with the use of stoichiometric amounts of chloride and hydride the  $\text{Al-H}$  absorption ( $\text{HAIR}_2 \cdot \text{R}_2\text{O}$ ) at  $1750\text{ cm}^{-1}$  disappears completely while the strong  $\text{Pb-H}$  absorption at  $1680\text{ cm}^{-1}$  appears. However, isolation of the tributyl hydrides by distillation before the hydrolysis of the dialkylaluminum chlorides is not possible, as this requires too high a temperature. Also, the hydrolysis is difficult. After addition of the reaction mixture to Seignette salt solution we obtained products which were either contaminated by  $\text{Al-C}$  groups or mainly—as a consequence of the back reaction—by organolead halides. Often the hydrides decompose during this work-up procedure.

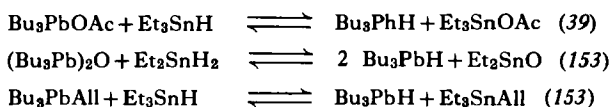
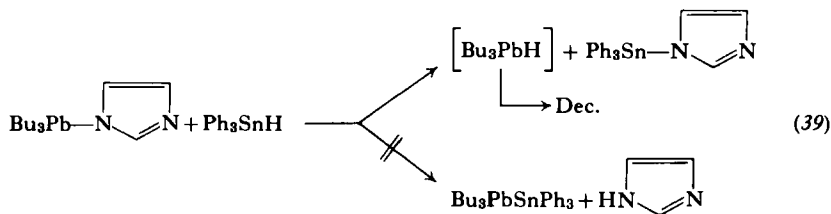
In general it can be said that aluminum organic reducing agents in organolead chemistry do not as yet show the same advantages which have been observed with organotin compounds.

e. *With Organotin Hydrides.* It is not possible to reduce organolead chlorides with tin hydrides or tin hydride chlorides, because the equilibrium for both reactions (188) lies far to the left.<sup>2</sup> (Compare the spontaneous reaction of  $\text{Et}_3\text{SnCl}$  with  $\text{Bu}_3\text{PbH}$ , Table IX.)

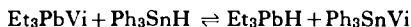
<sup>2</sup> On the contrary, the reduction of organolead chloride with organolead hydride is successful, if the hydride formed is the lowest boiling component and can be distilled off during the reaction. [Compare the corresponding reaction with the tin compounds (202).] Thus  $\text{Et}_3\text{PbH}$  is formed corresponding to the equation (188):  $\text{Et}_3\text{PbCl} + \text{Bu}_3\text{PbH} \rightleftharpoons \text{Et}_3\text{PbH} + \text{Bu}_3\text{PbCl}$ .



The same is true for  $\text{X} = \text{Br}$ ,  $\text{OR}$ ,  $\text{SR}$ , or aryl (39). Recently, both van der Kerk *et al.* (39) and Ourselves (198) found a procedure with which trialkyl hydrides can be prepared in situ ( $\text{X} = \text{halogen}$ ). In the cases where  $\text{X}$  is an acetate, imidazole (39),  $\text{OH}$  (respectively  $\text{OPbR}_3$ ), and allyl (198), the equilibrium is shifted more to the side of  $\text{R}_3\text{PbH}$ .

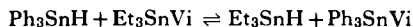


Organolead hydrides are more reactive towards  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  bonds than are the corresponding tin hydrides. Therefore, it is very easy to add lead hydrides completely to unsaturated compounds by placing the latter into the mixture of  $\text{R}_3\text{PbX}$  and organotin hydrides. Compare Section III, D,2. An analogous exchange of vinyl and hydrogen

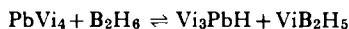


has not been observed; however even if it is slower than hydrogen-allyl exchange it must take place. There are two clear indications:

(1) Triphenyltin hydrides and triethyltinvinyl easily exchange  $\text{H}$  for  $\text{Vi}$  at room temperature, as was shown in a kinetic study (198).

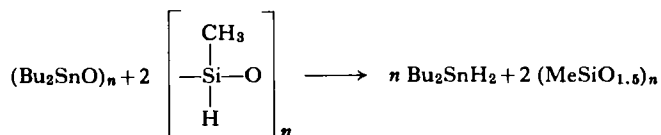


(2) Holliday and Pendlebury (113) recently showed that tetravinyllead exchanges one of its vinyl groups with hydrogen of diborane even at  $-78^\circ\text{C}$ .



f. *With Organosilicon Hydrides.* The reduction of plumboxanes with silicon hydrides appears to be promising, now that it has been shown that

stannoxanes and organotin alkoxides are easily and exothermically reduced by some silanes, especially by the commercially available polymeric silicon hydrides (101, 122).

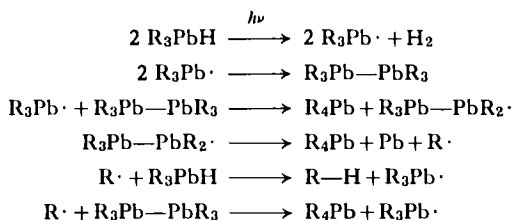


The use of the polymeric silicon hydrides could be of a special significance because a cross-linked product insoluble in organic solvents could easily be separated from  $\text{R}_3\text{PbH}$ .

## 2. Properties

a. *Stability and Decomposition.* The known organolead hydrides  $\text{R}_3\text{PbH}$  and  $\text{R}_2\text{PbH}_2$  are shown in Table VII. They decompose much below room temperature if  $\text{R} = \text{Me}$  or  $\text{Et}$ . The undiluted organolead hydrides with  $\text{R} > \text{Et}$  are stable up to about  $0^\circ \text{C}$  if air is carefully excluded. At  $20^\circ \text{C}$  most of them slowly decompose. Thus tripropyllead hydride still shows  $\text{Pb}-\text{H}$  absorption in the IR spectrum after 2 days. But when exposed to daylight some of the molecules, even with air excluded, decompose within 24 hr to  $\text{H}_2$ ,  $\text{C}_3\text{H}_8$ ,  $\text{Pb}$ ,  $\text{Pr}_4\text{Pb}$ , and  $\text{Pr}_6\text{Pb}_2$ . The propane probably arises from propyl radicals which are trapped by the hydride still available, before they are able to disproportionate to propane and propene. If the experiment was interrupted even earlier, besides unreacted  $\text{Pr}_3\text{PbH}$ ,  $\text{Pr}_6\text{Pb}_2$  and  $\text{H}_2$  were found almost exclusively. During the decomposition of  $\text{Me}_3\text{PbH}$ , Duffy *et al.* (53) detected only methane and no ethane. Thus all the methyl radicals seemed to be trapped by H abstraction before they are able to dimerize.

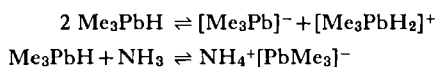
Assuming, as Becker and Cook (24) did, that the decomposition of the  $\text{Pb}-\text{H}$  bond starts with a homolysis, the following can be written:





$\text{NH}_3$  and amines also decompose the hydrides. If diethylamine is added to  $\text{Bu}_3\text{PbH}$  at  $20^\circ\text{C}$  the hydride reacts violently. At first  $\text{H}_2$  evolves, but with the aid of the large amount of heat which is set free in the undiluted mixture total decomposition takes place.

Similarly Holliday *et al.* (53) observed a greater lability of  $\text{Me}_3\text{PbH}$  in the presence of liquid  $\text{NH}_3$ . They interpreted the low-temperature NMR spectrum of  $\text{Me}_3\text{PbH}$  and of  $\text{Me}_3\text{PbH}$  in liquid  $\text{NH}_3$  according to the following equilibria:



But verification of the presence of a larger quantity of ionic particles as required by the equation is still missing. Certainly the concentration of ions in pure organolead compounds and in their solutions in nonpolar organic solvents such as benzene should be very small. The IR spectra can be interpreted in accordance with normal covalent  $\text{Pb—H}$  bonds.

b. *M—H Frequencies of the Group IVB Elements.* The organolead hydride frequencies can be classified along with those of the other Group IVB elements; see Table VIII.

TABLE VIII  
FREQUENCIES OF  $\text{R}_3\text{M—H}$  ( $\text{cm}^{-1}$ )

	Si (151)	Ge (181)	Sn (189)	Pb
$\text{Me}_3\text{MH}$	2118	2037	1837	1709 (9)
$\text{Et}_3\text{MH}$	2097	2006	1816	1689 (152)
$\text{Pr}_3\text{MH}$	2100	2003	1807	1675 (194)
<i>n</i> - $\text{Bu}_3\text{MH}$	2100	2003	1813	1680 (194)
Average values	2100	2000	1810	1680
Differences		100	190	130

All methyl-metal hydride absorptions lie at higher frequencies than those for compounds with longer alkyl substituents, which themselves show only small differences among their frequencies. Furthermore, the frequency difference between germanium and tin compounds is almost twice the amount ( $\sim 190$ ) between silicon and germanium or tin and lead compounds. With this fact in mind the pairs Si/Ge and Sn/Pb can be expected

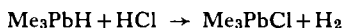
to have similar reactivities, but not the Ge/Sn pair. This is verified by several experiments. Many reactions which are not possible with Si or Ge can be smoothly performed with Sn and Pb (see e.g., Section III,D,4).

### B. Organolead Hydrides as Reducing Agents

All organolead hydrides are very sensitive to oxidation. Filter paper saturated with tributyllead hydride and exposed to air burns instantly. Organolead hydrides are much more reactive than the other hydrides of Group IVB.

#### 1. Standardization

The strong reducing property is suitable for a simple and accurate assay. Ethyl iodide in the absence of air and at  $-40^{\circ}$  to  $-60^{\circ}$  C is reacted in a Y-shaped tube connected with a gas buret (186) with the hydrides which are shown in Table VII. Upon warming to room temperature ethane is formed quantitatively so that the amount of hydride is easily determined (152, 188). We used this procedure as a standard method, always obtaining reliable results, and it was also used for the experiments described below. Holliday *et al.* (53) determined the amount of  $\text{Me}_3\text{PbH}$  by reacting the hydride at  $-112^{\circ}$  C with HCl and measuring the amount of  $\text{Me}_3\text{PbCl}$  or  $\text{H}_2$  formed.



However, even at  $-78^{\circ}$  C substantial amounts of  $\text{CH}_4$  and dimethyllead dichloride are obtained with the latter method.

Halide, carbonyl, nitro, and nitroso compounds were reacted with tributyllead hydride (12, 152, 187, 188) in order to compare the reducing properties of the organolead hydrides of Group IVB more closely.<sup>3</sup> The results are shown in Table IX.

All reductions were made at  $0^{\circ}$  and  $20^{\circ}$  C respectively. Higher temperatures are not possible in view of the instabilities of the hydrides. Therefore, slow reactions cannot be accelerated by raising the temperature. The reducing ability of organolead hydrides toward halogen compounds decreases from the iodides to the chlorides (Table IX). Iodobenzene

<sup>3</sup> There is a review of reductions with the help of organotin hydrides by Kuivila (156).

TABLE IX  
REDUCTION WITH TRIBUTYLLEAD HYDRIDE <sup>a</sup>

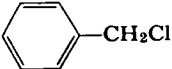
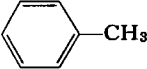
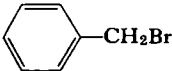
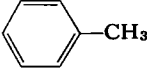
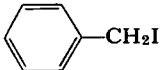
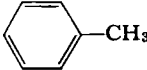
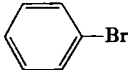

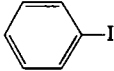

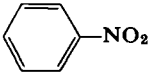
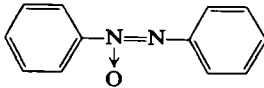
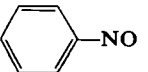
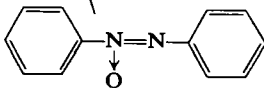
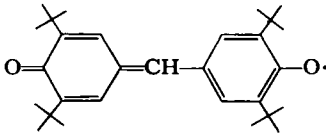
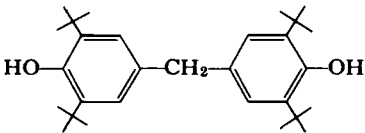
No.	Compound	Mole ratio	Conditions <sup>b</sup> (°C)	Product	Yield (%)
1	CH <sub>3</sub> I	1:1	0°, ex	CH <sub>4</sub>	100
2	C <sub>2</sub> H <sub>5</sub> I	1:1	0°, ex	C <sub>2</sub> H <sub>6</sub>	100
3		1:1	0°, 27 hours		70
4		1:1	0°, ex		60
5		1:1	0°, ex		80
6		1:1	+ 0°, 5 days 20°, 3 days		60
7		1:1	0°, ex		50
8	Br—CH <sub>2</sub> —CH <sub>2</sub> —Br	2:1	0°, ex	H <sub>2</sub> C=CH <sub>2</sub> ; H <sub>2</sub>	95
9	CH <sub>2</sub> —CH—CH <sub>2</sub> Br	1:1	0°, ½ hr	CH <sub>2</sub> —CH—CH <sub>3</sub>	95
10	CH <sub>3</sub> —CH—CH—CH <sub>2</sub> Br	1:1	0°, ½ hr	Butene	80

TABLE IX—*continued*

No.	Compound	Mole ratio	Conditions (°C)	Product	Yield (%)
11	<chem>CCl4</chem>	1:1	0°, ex	<chem>HCCl3</chem> ; <chem>H2CCl2</chem>	75 + 5
12	<chem>c1ccccc1CCl3</chem>	1:1	0°, ex	<chem>c1ccccc1CHCl2</chem>	90
13	<chem>c1ccccc1C(=O)CH2Br</chem>	1:1	0°, 1 hr	<chem>c1ccccc1C(=O)CH3</chem>	90
14	<chem>c1ccccc1C(=O)CH3</chem>	1:1	20°, 2 days	<chem>c1ccccc1C(O)CH3</chem>	25
15	<chem>c1ccccc1CHO</chem>	2:1	20°, ex	<chem>c1ccccc1CH2OH</chem>	100

16	$\text{CH}_3-\text{C}(=\text{O})-\text{C}_2\text{H}_5$	1:1	0°, 2 days	$\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{C}_2\text{H}_5$	10
17	$\text{CH}_3-\text{CH}_2-\text{CHO}$	2:1	0°, ex	$\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$	100
18	$\text{CH}_3-\text{COCl}$	1:1	0°, ex	$\text{CH}_3-\text{COOC}_2\text{H}_5$	50
19		4:1	0°, 20 hr		10
20		2:1	0°, ex		80
21		4:1	0°, ex		100
22	$\text{Et}_3\text{SnCl}$	1:1	0°, $\frac{1}{2}$ hr	$\text{Et}_3\text{SnH}$	55

<sup>a</sup> References (12), (152), (188), and (194).

<sup>b</sup> ex = exothermal reaction.

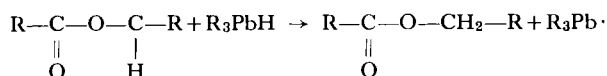
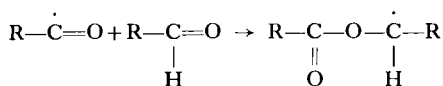
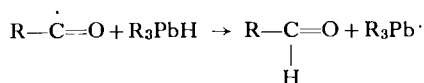
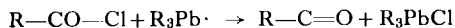
(compound 7 in Table IX) reacts violently with  $\text{Bu}_3\text{PbH}$ ; a smooth reaction without Pb separation is obtained in solution. Bromobenzene (6) is not reduced for several days, and chlorobenzene under the same conditions is not reduced at all. The relations are similar with the benzyl halides (3–5). Aliphatically bound halogen (1–5) is eliminated more readily than aromatically bound (6–7). The 1,2-dihalogen compounds (8) yield the corresponding olefins. In the case of unsaturated halogenides (9, 10) halogen is eliminated without adding the organolead hydride to the double bond or reducing the double bond. As expected the polyhalogen compounds (11, 12) react even more vigorously than the monohalides; depending on the mole ratio used, one to three of the chlorine atoms are replaced stepwise by H. In this case the experiments must be done in solution; otherwise the reaction mixture explodes. Aldehydes (15, 17) are instantaneously reduced to alcohols; no addition to the carbonyl double bond was observed. Ketones (14, 16) on the other hand react very slowly, and in  $\alpha$ -bromoketones (13) the bromine is substituted by hydrogen. Acetyl chloride (18) is reduced to ethyl acetate. Nitrobenzene (19) gives azoxybenzene, but the formation of azobenzene cannot be excluded because the unfavorable proportion of the hydride and nitro compounds renders the work-up difficult. Nitrosobenzene (20) gives only azoxybenzene. From galvinoxyl (21), (19), the corresponding phenol is instantaneously formed.

The results of the last two experiments are of great importance. They show clearly that the lead hydrides have a higher reduction potential than the tin hydrides: galvinoxyl (21) is not reduced by triethyltin hydride even at  $70^\circ\text{--}80^\circ\text{C}$  (255), but is reduced by tributyllead hydride spontaneously at  $0^\circ\text{C}$ . Finally, triethyltin chloride (22) can be reduced by tributyllead hydride. (Under the same conditions reduction of triethylgermanium chloride with tributyltin hydride also takes place spontaneously.)

In view of the exothermic reduction of alkyl iodides by  $\text{Bu}_3\text{PbH}$  (1, 2) and by  $\text{Bu}_3\text{SnH}$  (156), while their reduction with  $\text{Bu}_3\text{GeH}$  requires refluxing for several hours (240), it is possible, at least for the elements Ge/Sn/Pb, to establish the increase of reduction power of the hydrides,  $\text{R}_3\text{MH}$ .

## 2. Reaction Mechanism

The reduction of acetyl chloride (18) may follow a radical mechanism. If one transcribes the pattern which was shown for the analogous reduction with  $n\text{-Bu}_3\text{SnH}$  by Kuivila *et al.* (158), the following scheme results:



A radical mechanism may also be proposed for the other reductions, at least for the alkyl and aryl halides in view of the clarified relations of their reduction with organotin hydrides (156). For carbonyl or other unsaturated compounds (Table IX), a polar mechanism is also possible; it could be of  $\text{S}_{\text{N}}2$  type. Further experiments are needed for clarification.

### C. Reactions with Diazoalkanes

The organolead hydrides, like those of Si, Ge (147), and Sn (164, 240), react with diazoalkanes between  $-80^\circ$  and  $0^\circ \text{C}$  (24) (Table X). (The values

TABLE X

Hydrides	Diazoalkanes	Products obtained (wt %)				
		$\text{Me}_4\text{Pb}$	$\text{Me}_3\text{PbEt}$	$\text{Me}_2\text{PbEt}_2$	$\text{MePbEt}_3$	$\text{Et}_4\text{Pb}$
$\text{Me}_3\text{PbH}$	$\text{C}_2\text{H}_4\text{N}_2$	(89)	11	—	—	—
$\text{Me}_2\text{PbH}_2$	$\text{C}_2\text{H}_4\text{N}_2$	(83)	12	5	—	—
$\text{Et}_3\text{PbH}$	$\text{CH}_2\text{N}_2$	—	—	—	31	(69)
$\text{Et}_2\text{PbH}_2$	$\text{CH}_2\text{N}_2$	—	—	2	1	(97)

in parentheses are for the disproportionation products of lead hydrides; only the values not in parentheses indicate the immediate reaction products.)

### D. Hydroplumbation of Unsaturated Compounds

#### 1. Unactivated Olefins

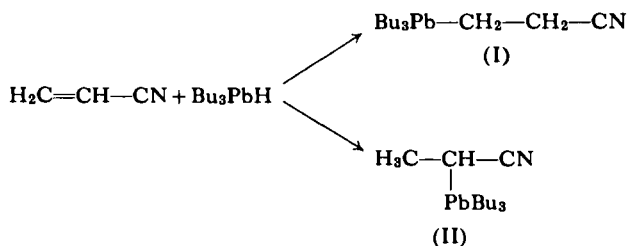
We did not succeed in reacting olefins containing isolated double bonds, i.e., 1-octene, allyl alcohol, or allyl acetate at  $0^\circ$  or  $20^\circ \text{C}$  with  $\text{Bu}_3\text{PbH}$

(152, 188). Radical formers as catalysts were of no help; they mostly accelerated the decomposition of  $\text{Bu}_3\text{PbH}$ . Also catalysis by aluminum alkyls (189, 201), used for the addition of organotin hydrides to olefins, is not useful because the transfer of an alkyl group to  $\text{R}_3\text{PbH}$  depends upon the necessary addition of  $\text{R}_2\text{AlH}$  to the olefin (189, 284) at  $20^\circ\text{C}$  (which is the limit for the stability of the organolead compounds used) and this does not take place.

However, Becker and Cook (24) report addition of  $\text{Me}_3\text{PbH}$  to ethylene at  $0^\circ\text{C}$  in diglyme at 2.5 atmospheres. They estimate a yield of 92% of  $\text{Me}_3\text{PbEt}$  by gas chromatography. Later Duffy *et al.* (53) tried the same reaction in dimethyl ether between  $-78^\circ$  and  $0^\circ\text{C}$  and at about normal pressure. The desired adduct was not formed, and ethylene was quantitatively recovered. It is of interest in this connection that a patent has been issued for the addition of organolead hydrides to ethylene, propylene, isobutylene, cyclohexene, and other  $\alpha$ -olefins (27).

## 2. Activated Olefins

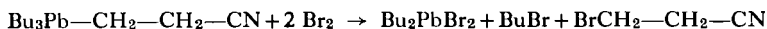
In all known examples organolead hydrides add smoothly to olefins which have their  $\text{C}=\text{C}$  bond conjugated to another unsaturated group. The adduct was obtained in good yields when acrylonitrile was dropped with stirring into  $\text{Bu}_3\text{PbH}$  in ether at  $0^\circ\text{C}$  (12, 152, 188, 194). It can be distilled under vacuum without decomposition (b.p.  $116^\circ\text{--}119^\circ/0.01$  torr). But if  $\text{Bu}_3\text{PbH}$  and acrylonitrile are poured together without dilution, after a certain incubation time an extremely violent reaction occurs. Most of the lead hydride decomposes and the olefin is polymerized. There are two possibilities for the products of the above-mentioned smooth reaction in diluted solutions, (I) or (II).



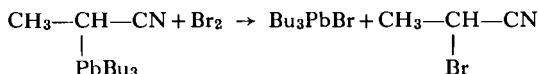
To clarify this question we degraded the adduct with  $\text{Br}_2$  in  $\text{CCl}_4$  at  $-70^\circ$  to  $20^\circ\text{C}$  and the cleavage fragments were investigated gas chromatographically. Besides *n*-butyl bromide only  $\beta$ -bromopropionitrile was



detected (199). Thus (I) must be the right structure, which is degraded as follows:

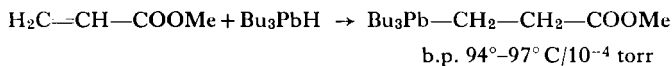


If (II) was the right structure, the propionitrile group would have cleaved preferentially because the plumbyl group is allylic to the nitrile group (see Section II,D,1). The  $\alpha$ -bromopropionitrile which would be expected in this case was not present, as determined gas chromatographically.

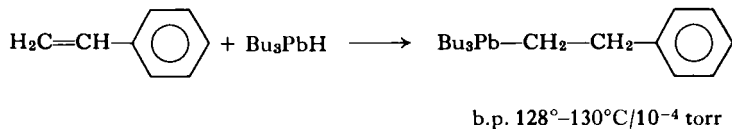


But 2% of an authentic sample, mixed with the reaction mixture, was detected without any doubt.

The methyl ester reacts similarly to acrylonitrile.



Styrene reacts somewhat more slowly.



The mechanism is discussed in Section III,E.

### 3. Alkynes

As is true for hydrostannation, acetylenes are also more reactive than the olefins toward hydroplumbation. Acetylenedicarboxylic acid dimethyl ester and ethyl propiolate (152) add  $\text{Bu}_3\text{PbH}$  at  $-50^\circ \text{C}$  (used as a pure substance, or made in situ from organotin hydrides) spontaneously and without side reactions.  $\text{Me}_3\text{PbH}$  adds in the same smooth manner to cyanoacetylene and methyl propiolate (165). Phenylacetylene reacts under the same conditions but in a side reaction Pb is precipitated and  $\text{H}_2$  evolves. After a short while starting materials disappear if excess of lead hydride is used. The IR spectrum shows absorption at  $990 \text{ cm}^{-1}$ , which is in accordance with a trans adduct (152, 194).



Leusink and van der Kerk (165) showed in another example that the cis adduct could be formed first, and then rearrange under the influence of

$R_3PbH$  to the trans adduct. On warming from  $-70^\circ$  to  $0^\circ C$  the mixture of 91% *cis*- $\beta$ -, 9% *trans*- $\beta$ - $Me_3Pb-CH=CH-CN$  and 15 mole %  $Me_3PbH$  changed to a ratio of 54% *cis*- $\beta$  and 46% *trans*- $\beta$ .

#### 4. Alkylidenemalonodinitrile and Ethyl Cyanoacetate

The alkylidenemalonodinitriles shown in Table XI react exothermically in benzene at  $20^\circ C$  with a stoichiometric amount of  $n-Bu_3PbH$  to give yellowish, viscous 1:1 adducts. No decomposition of the lead hydride

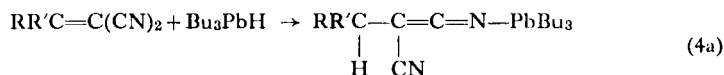
TABLE XI  
SPECTROSCOPIC DATA FOR EQ. (4a)<sup>a</sup>

Reactant	Adduct			Product of hydrolysis of the adduct
$RR'C=C(CN)_2$	$RR'-CH-C \begin{array}{l} \nearrow C=N-PbR_3 \\ \searrow CN \end{array}$			$RR'CH_2-CH(CN)_2$
	$\nu(CN)$ ( $cm^{-1}$ )	$\nu(CN)$ ( $cm^{-1}$ )	$\nu(C=C=N)$ ( $cm^{-1}$ )	$\nu(CN)$ ( $cm^{-1}$ )
 $-CH=C(CN)_2$	2210	2170	2070	2260
$CH_3-CH=C(CN)_2$	2230	2165	2070	2240
 $-CH=C(CN)_2$	2220	2160	2070	—

<sup>a</sup> References (152), (195).

occurs during the reaction (195). Because of their thermal instability these adducts cannot be purified by distillation.

The IR spectrum of the adduct differs from those of the reactants in an intense nitrile absorption with a bathochromic shift and a very strong absorption at  $2070\text{ cm}^{-1}$  which is characteristic for the cumulated double bond ( $-C=C=N-$ ). Therefore it can be deduced that a 1,4-addition to the conjugated system to form *N*-plumbylketeneimines takes place.



(That the 1,2-adduct is also formed in small amounts has not yet been excluded.) On the other hand acrylonitrile reacts as mentioned only with the C=C double bond and no keteneimine absorption could be detected in the IR spectrum of this adduct.

Neumann *et al.* (204) were the first to accomplish analogous reactions with  $R_3SnH$ . Up to now all attempts to add silicon or germanium hydrides ( $R_3MH$ , where  $R = Et, C_6H_5$ ) to benzylidenemalonodinitrile have failed. The analogous 1,4-additions with Grignard compounds have been known for a long time (223a).

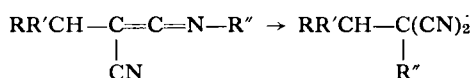


In some cases similar structures are discussed for corresponding lithium organic compounds. But from a preparative point of view the lead hydride adducts cannot be compared to these metal organic adducts because the former give on hydrolysis the hydrated reactants, the latter the alkylated reactants.

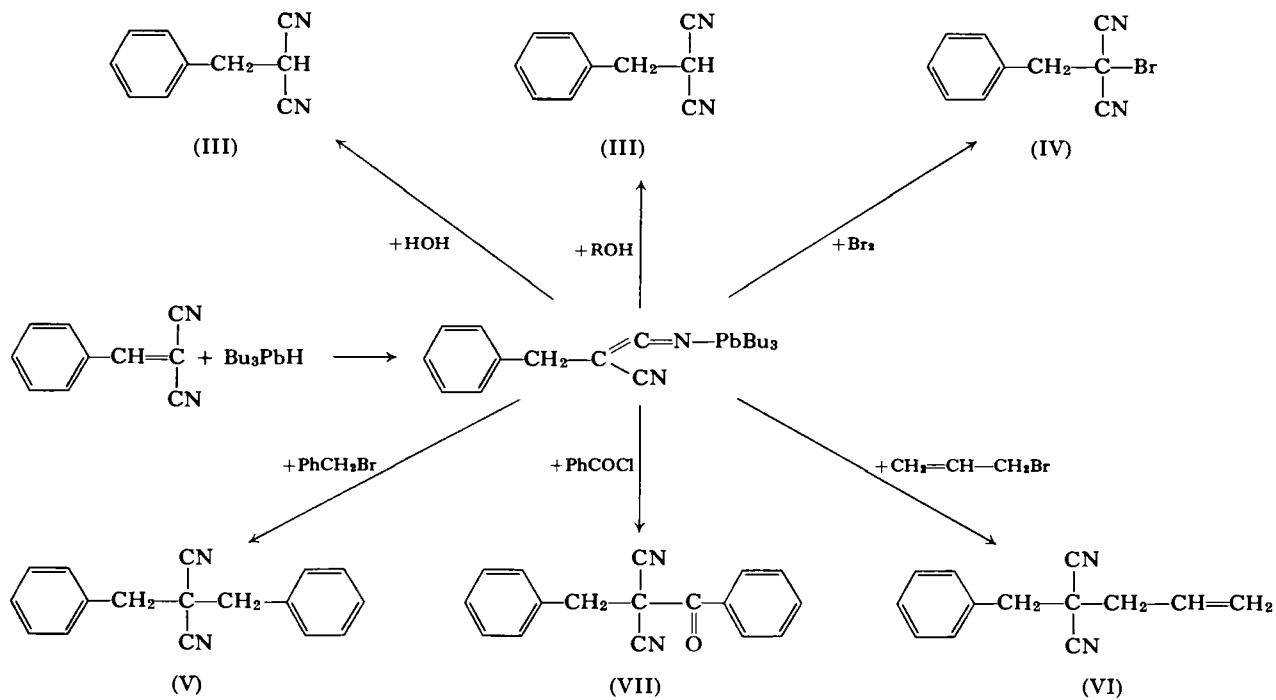
The reactions of the keteneimines are in accordance with their structure (195). Water and alcohol spontaneously yield the hydrated product (III), while bromine gives brominated reactants (IV). With benzyl bromide, allyl bromide, and benzoyl chloride the C-alkylated and the C-acetylated compounds (V)–(VII) are exothermically formed in good yields. On the other hand isobutyl bromide reacts, if at all, only very slowly; it is necessary to heat for several days to 60° C, whereby the keteneimines are decomposed.

Toward organic halides the lead keteneimines show a graduated reactivity, which was also observed with the ketene acetals (free of lead). For  $CH_2=C(OR)_2$  the reactivity varied with R as follows (68):  $R = \text{benzyl} > \text{allyl} > \text{isobutyl}$ . The reactions of the 1:1 adducts are probably 1,2-additions to the C=C double bond with a succeeding  $\beta$ -elimination of  $Bu_3PbX$ .

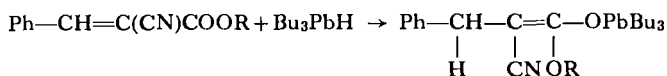
If a primary attack on the Pb—N bond forming the N-alkylated keteneimine is assumed, a migration of the alkyl substituent would have to take place.



The analogous nitrile esters and derivatives of cyanoacetic acid,  $RR'C=C(CN)COOR$  (195) react similarly to the dinitriles. The weaker



— I effect of the ester grouping together with the stronger one of the nitrile grouping is still capable of polarizing the  $C\equiv C$  group sufficiently (i.e., in isobutyronitrile as a solvent).

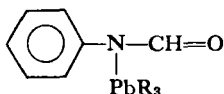


In nonpolar solvents such as benzene, partial radical 1,2-addition to the  $C\equiv C$  group takes place.

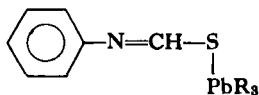
### 5. Isocyanates and Isothiocyanates

The reaction of phenyl isocyanate with  $\text{Bu}_3\text{PbH}$  at  $-70^\circ\text{C}$  leads to a 1,1-adduct, which hydrolyzes very easily to  $\text{Bu}_3\text{PbOH}$  and formanilide (194). (If the organolead hydride contains traces of  $\text{Pb}-\text{O}$  compounds polymerization of  $\text{PhNCO}$  takes place as a side reaction.)

For the adduct, as in the case of the analogous tin adduct (208), the structure of an *N*-plumbylformanilide can be accepted.



The  $\text{Pb}-\text{N}$  bond undergoes further reaction with  $\text{Bu}_3\text{PbH}$  with cleavage and formation of diplumbane and with  $\text{PhNCO}$  by addition (Section IV). Phenyl isothiocyanate,  $\text{PhNCS}$ , reacts with  $\text{Bu}_3\text{PbH}$  at  $0^\circ\text{C}$  without gas evolution or  $\text{Pb}$  precipitation. The  $\text{NCS}$  absorption ( $2080\text{ cm}^{-1}$ ) and the  $\text{Pb}-\text{H}$  absorption ( $1680\text{ cm}^{-1}$ ) disappear as rapidly as the hydride is added. A yellow, foul smelling, oily 1:1 adduct is obtained (152). The structure (VIII) of the adduct



(VIII)

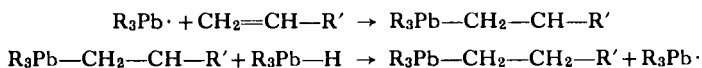
follows from the absence of  $\text{N}-\text{H}$  absorption, from the very slow hydrolysis by water (no presence of a  $\text{Pb}-\text{N}$  bond), and from the fast hydrolysis by aqueous acid to thioformanilide. It is known that the  $\text{Pb}-\text{S}$  bond is very resistant to hydrolysis (2). The IR spectrum of (VIII) is very similar to that of the corresponding tin adduct (208).

Butyl isothiocyanate reacts with  $\text{Bu}_3\text{PbH}$  at  $0^\circ\text{C}$  without precipitation of lead. After 3 hours the lead hydride is used up but not the isothiocyanate. The smell of isonitrile and the strong absorption in the  $\text{N—H}$  region at  $3220\text{ cm}^{-1}$  make it probable that reduction is the main reaction. The 1:1 adduct could not be isolated (152).

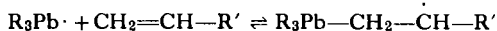
### E. Mechanism of the Hydroplumbation

Experience with organotin hydrides (189), the longer distance of the  $\text{Pb—H}$  bond compared to the  $\text{Sn—H}$  bond, and the low dissociation energy and the good polarizability of the  $\text{Pb—H}$  bond (see Section I,B) suggest that hydroplumbation can follow a radical as well as a polar mechanism. It is important for the *radical reaction* that the organolead compounds be capable of forming initiating radicals even at  $0^\circ\text{—}20^\circ\text{C}$ , without air, and in diffuse daylight, by homolytical cleavage of the  $\text{Pb—H}$  bond.

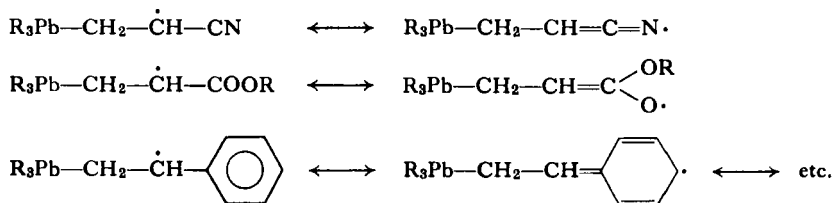
While tributyltin hydride (not a radical former) undergoes no addition to acrylonitrile at  $0^\circ\text{C}$  in 5 hr without a catalyst, addition in the case of tributyllead hydride is complete under the same conditions and gives the  $\beta$ -adduct (I) (194). Thus after the starting radicals are formed, a radical chain reaction takes place which can be formulated as follows:



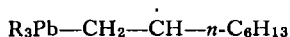
The analogous attack of a tin radical on an olefin is reversible (191). Because the energy of dissociation of a  $\text{Pb—C}$  bond (31 kcal/mole) is at least 15 kcal/mole lower than that of the  $\text{Sn—C}$  bond the reversibility of the reaction is even more probable in the case of lead than with tin.



Experiments which could prove this statement are apparently not yet known. Because the gain in energy with the formation of a  $\text{Pb—C}$  bond (31 kcal/mole, see Section I,B) is relatively small, only those  $\text{C=C}$  groups can be attacked whose  $\pi$ -bond cleavage generates mesomerically stabilized radicals (compare the general statements in Stirling, 260), i.e.,

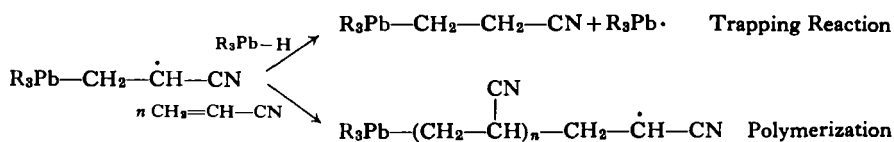


The reaction does not occur if the intermediate radicals are energy-rich and not stabilized, e.g.,



The “ $\pi$ -bond cleavage energy” for ethylene is reported to be 58 kcal/mole (260) and should be about the same for 1-octene. The addition of a plumblyl radical would be (58 – 31 = 27 kcal/mole) very endothermic and therefore does not take place. Thus it can be explained that acrylonitrile, acrylic esters, and styrene can take part in the hydroplumbation, but not 1-octene.

Furthermore, it is evident that attack of plumblyl radicals on olefins gives only  $\beta$ -adducts. If  $\text{R}_3\text{Pb}\cdot$  would attack the  $\alpha$ -position, the energetically very unstable radicals (no mesomeric stabilization)  $\cdot\text{CH}_2-\text{CH}(\text{PbR}_3)\text{R}'$  ( $\text{R}' = \text{CN}, \text{COOR}, \text{Ph}$ ) would be formed. The possibility of polymerizing acrylonitrile in the presence of organolead hydrides is worth attention (see Section III,D,2). The latter, in spite of the better energy balance, 10 kcal/mole, are far poorer radical trapping agents than the corresponding organotin hydrides (189). Attack on further olefin molecules can successfully compete with the trapping reaction if the proper experimental conditions are chosen. This leads to polymerization.



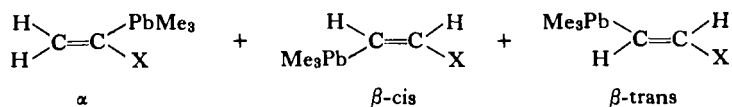
Thus far we have dealt with olefins. But hydroplumbation of alkynes in nonpolar solvents also follows a radical mechanism, as was shown by Leusink and van der Kerk (165).

A precise proof for the radical mechanism by using galvinoxyl, as effected in the case of hydrostannation (189, 203), cannot be given here, because galvinoxyl is reduced by organolead hydride even at 0° C, see Table IX.

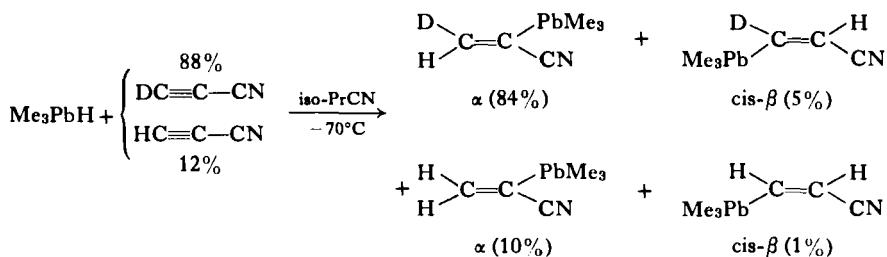
As mentioned above, organolead hydrides are also capable of undergoing *polar reactions*. That this is true can be observed in the hydroplumbation of alkynes (195), where during the addition of  $\text{Me}_3\text{PbH}$  to cyanoacetylene in diethyl ether the  $\beta$ -adducts (cis and trans) are formed almost exclusively, whereas 76% of  $\alpha$ -adduct is formed in butyronitrile as solvent, probably by means of an ionic reaction (Table XII.)

TABLE XII  
ADDITION OF  $\text{Me}_3\text{PbH}$  TO  $\text{HC}\equiv\text{C}-\text{CN}$  AND  $\text{HC}\equiv\text{C}-\text{COOMe}$

X	Adduct	In ether	In butyronitrile
CN	$\alpha$	2%	76%
COOMe	$\alpha$	—	15%
CN	$\beta$ -cis	92%	24%
COOMe	$\beta$ -cis	—	80%
CN	$\beta$ -trans	6%	—
COOMe	$\beta$ -trans	—	5%



The dependence of the  $\alpha/\beta$  ratio on the polarity of the solvent used suggests a radical mechanism for formation of the  $\beta$ -adducts and a polar mechanism for the  $\alpha$ -adducts (165). Both the  $\alpha$ - as well as the  $\beta$ -adducts are formed by trans addition. This can be shown by (1) the structure of the product of  $\alpha$ -addition of  $\text{Me}_3\text{PbH}$  to deuterated organoacetylenes:



and (2) the great yield (92%) of cis- $\beta$ -adduct in the addition of  $\text{Me}_3\text{PbH}$  to cyanoacetylene (see Table XII).

The same facts are known for hydrostannation (165a). The polar mechanism is very greatly favored in the strongly polar systems of alkylidene-malonodinitriles (IX) and cyanoacetic esters (X) which are discussed in Section III,D,4 (195).

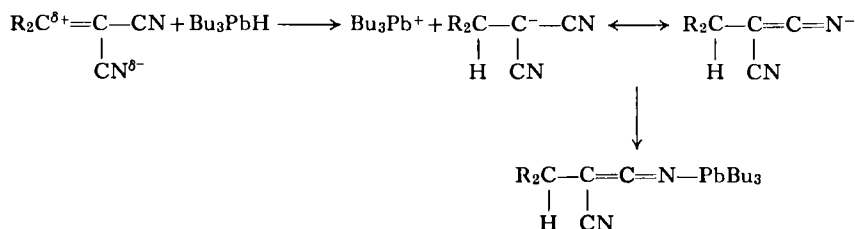


$$\begin{array}{c} \text{R}' \quad \delta^+ \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{R} \quad \delta^- \end{array} \begin{array}{l} \text{C}\equiv\text{N} \\ \text{C}\equiv\text{N} \end{array} \quad \delta^-$$

(IX)

$$\begin{array}{c} \text{R}' \delta^+ \\ \diagdown \\ \text{C} = \text{C} \begin{array}{l} \diagup \text{COOR} \\ \diagdown \text{C} \equiv \text{N} \end{array} \delta^- \\ \diagup \\ \text{R} \end{array} \quad (\text{X})$$

The strong  $-I$  effect of the nitrile and ester groupings causes a definite partial positive charge on the other end of the conjugated system, which is the C atom. In accordance with the clear arguments used for the addition of organotin hydrides to such systems (204) it can be assumed that in the case of  $R_3PbH$  the primary step is a nucleophilic attack of the hydride hydrogen on the positive C atom, i.e.,



The mesomeric anion is stabilized to the keteneimine or ketene acetal derivative. But in cases with weaker  $-I$  effects, a radical 1,2-addition to the  $C=C$  group is able to compete (see Section III,D,4).

## IV

### THE Pb—N BOND

### A. Preparation and Reactivity of Aminolead Compounds

## 1. Preparation

Until recently only a few compounds possessing a Pb—N bond have been known [review up to 1963 (174)], mainly imido and sulfonamido compounds which were prepared by reacting the acidic N—H compounds with organolead hydroxides or oxides (Table XIII), i.e.,

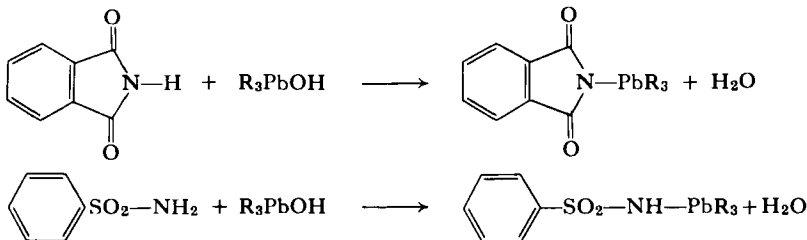


TABLE XIII  
 PLUMBYL AMINES AND AMIDES

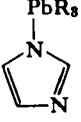



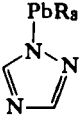

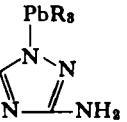
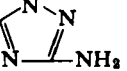

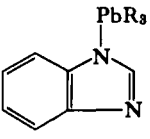
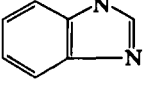
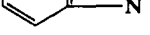
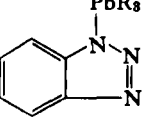
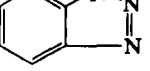
Compound	Method <sup>a</sup>	Properties (M.p., °C)	References
Et <sub>3</sub> PbNEt <sub>2</sub>	A	Oil	152, 196
Pr <sub>3</sub> PbNEt <sub>2</sub>	A	Oil	152, 196
Bu <sub>3</sub> PbNEt <sub>2</sub>	A	Oil	152, 196
iso-Bu <sub>3</sub> PbNEt <sub>2</sub>	A	Oil	152, 196
cyclo-Hex <sub>3</sub> PbNEt <sub>2</sub>	A	(Only in solution)	152, 196
Ph <sub>3</sub> PbNEt <sub>2</sub>	A	Crystalline	152, 196
Ph <sub>2</sub> Pb(NEt <sub>2</sub> ) <sub>2</sub>	A	(Only in solution)	152, 196
Et <sub>3</sub> PbNHCH <sub>2</sub> CHMeEt	A	Liquid	223
Me <sub>3</sub> PbN(SiMe <sub>3</sub> ) <sub>2</sub>	A	B.p. 85°–87° C/3 mm	243
Me <sub>3</sub> PbNMeGeMe <sub>3</sub>	B	B.p. 49° C/2 mm	239
 $\text{PbR}_3$ R = Et	D	100°	274
 $\text{PbR}_3$ R = Bu	D	48°–50°	274
 $\text{PbR}_3$ R = iso-Bu	D	167°	274
 $\text{PbR}_3$ R = Ph	D	285°	274
 $\text{PbR}_3$ R = Et	D	—	274
 $\text{PbR}_3$ R = Ph	D	265°	274
 $\text{PbR}_3$ R = Et	D	178°–181°	274
 $\text{PbR}_3$ R = Bu	D	116°–118°	274
 $\text{PbR}_3$ R = Ph	D	248°–256°	274
 $\text{PbR}_3$ R = Et, R' = H	D	189°–191°	274
 $\text{PbR}_3$ R = Bu, R' = H	D	104°–105°	274
 $\text{PbR}_3$ R = Ph, R' = H	D	270°	274
$\text{PbR}_3$ R = Bu, R' = SH	D	61°	274
 $\text{PbR}_3$ R = Bu	D	103°	274
 $\text{PbR}_3$ R = Ph	D	275°–276°	274
Ph <sub>3</sub> PbN <sub>3</sub>	F	—	166, 167
Me <sub>3</sub> PbNH <sub>2</sub> CN	D	126°–127°	274
Bu <sub>3</sub> PbNH <sub>2</sub> CN	D	Oil	274

TABLE XIII—continued

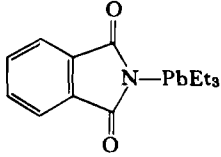
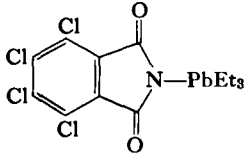
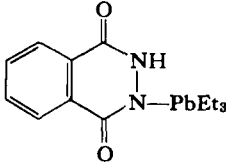
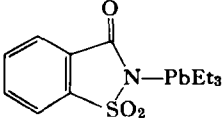
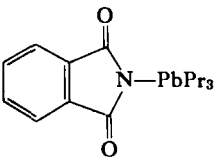
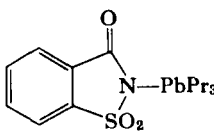
Compound	Method <sup>a</sup>	Properties (M.p., °C)	References
Et <sub>3</sub> PbNHSO <sub>2</sub> Me	E	97°	241
Et <sub>3</sub> PbNPhSO <sub>2</sub> Me	E	115.5°	241
Et <sub>3</sub> PbNHSO <sub>2</sub> Ph	A	132°	241
Et <sub>3</sub> PbNHSO <sub>2</sub> - <i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	E	133°	241
Et <sub>3</sub> PbNHSO <sub>2</sub> - <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	A, E	127°	241
Et <sub>3</sub> PbN( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )SO <sub>2</sub> - <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	E	111.5°	241
Et <sub>3</sub> PbN( <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> )SO <sub>2</sub> - <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	E	117°	241
Et <sub>3</sub> PbNHSO <sub>2</sub> - <i>p</i> -H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	E	171°	241
Et <sub>3</sub> PbNPhSO <sub>2</sub> CH=CH <sub>2</sub>	A	116°	241
Et <sub>3</sub> PbNPhSO <sub>2</sub> - <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	E	134°	241
Pr <sub>3</sub> PbNHSO <sub>2</sub> Me	E	67°	241
Pr <sub>3</sub> PbNHSO <sub>2</sub> Ph	E	96°	241
Pr <sub>3</sub> PbNHSO <sub>2</sub> - <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	A	100°	35
Pr <sub>3</sub> PbN( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )SO <sub>2</sub> - <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	E	123°	241
Pr <sub>3</sub> PbNHSO <sub>2</sub> - <i>p</i> -H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	E	101°	35
Pr <sub>3</sub> PbNPhSO <sub>2</sub> - <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	E	104°	35
(Et <sub>3</sub> PbNPhSO <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	E	180°, dec. 71°	241
Et <sub>2</sub> PrPbNHSO <sub>2</sub> - <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	A, E	94.5°	35, 103
	D	131°	102, 169
	D	—	169
	C	—	168
	E	135°	241

TABLE XIII—continued

Compound	Method <sup>a</sup>	Properties (M.p., °C)	References
	D	Crystalline	102, 169
	E	130°	241

<sup>a</sup> A,  $R_3PbCl + R'_2NM \rightarrow R_3Pb-NR'_2$ ; M = Na, Li.

B,  $R_3PbCl + R'_2NH \rightarrow R_3Pb-NR'_2$ .

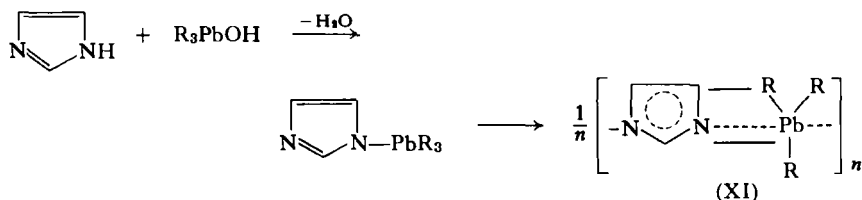
C,  $R_3PbCl + (R'-CO-NH-)_2 \xrightarrow{NaOH} R_3Pb-N(CO-R')-NH-COR'$

D,  $R_3PbOH + R'-CO-NH-R'' \rightarrow R_3Pb-NR''-COR'$ .

E,  $R_3PbOH + R'-SO_2-NHR'' \rightarrow R_3Pb-NR''-SO_2R''$ .

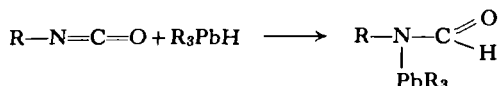
F,  $R_3PbOH + HN_3 \rightarrow R_3PbN_3$ .

Willemsens and van der Kerk (274) applied this method in 1965 to the N-heterocyclic compounds containing N—H groups. In this manner several N-plumbylheterocyclic compounds were produced (see Table XIII), e.g.,

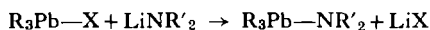


In some cases organolead halides can be used instead of the hydroxides or oxides, mainly if the hydrochloric acid formed is neutralized by an excess of amine (239, 243).

Recently we made a totally different approach (194, 195) by trying the addition of organolead hydrides to N-containing unsaturated systems, such as isocyanates and alkylidenemalonodinitriles, whereby the N-plumbyl alkylformamides and N-plumbyl keteneimines were formed (for further details see Section III,D,4,5).



Aminolead compounds of the simplest types,  $\text{R}_3\text{PbNR}'_2$  with, e.g.  $\text{R}' = \text{Me}, \text{Et}$  have recently been synthesized. Using the procedure which has been successful for the synthesis of aminotin compounds (126) these compounds were obtained without difficulty (152, 196) from lithium dialkylamides and organolead halogenides (Table XIII).



When petroleum ether is used as the solvent the insoluble  $\text{LiX}$  precipitates and can easily be separated by filtration. But if the organolead halogenide is insoluble in petroleum ether the solvent is mixed with either ether or THF.

The standardization of these very sensitive plumbylamines is made possible by removing the solvent and some remaining traces of  $\text{HNR}_2$  (present on account of undesirable hydrolysis) by vacuum. A sample is then examined for the presence of  $\text{Li}$  and  $\text{X}$ , weighed, and heated with an excess of dilute  $\text{NaOH}$ . The amine is then distilled as in the Kjeldahl analysis with 0.1  $N$   $\text{HCl}$  and back-titrated with 0.1  $N$   $\text{NaOH}$ .

## 2. Reactivity

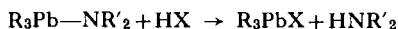
The  $\text{Pb}-\text{N}$  bond is highly reactive. Plumbylamines of the simplest type,  $\text{Bu}_3\text{Pb}-\text{NEt}_2$ , are very susceptible to hydrolysis and are slowly decomposed at  $20^\circ\text{C}$ . Therefore they cannot be purified by distillation and should be prepared just before use (Section IV, B). On the other hand, the  $N$ -plumbyl-carboxylic acids and sulfonic acid amides are stable towards moisture and can be crystallized (Table XIII).

It is surprising that some special  $N$ -plumbyl nitrogen heterocyclic compounds are quite stable towards hydrolysis; see structure (XI). If there is an additional nitrogen atom in the heterocyclic compound in the 3-position to the  $\text{NH}$  group, it assumes the role of an electron donor for a second molecule of the plumbylamine. The lead atom goes into the penta-coordinated state (174) and thus the  $\text{Pb}-\text{N}$  group is stabilized. It seems to be that all of the conclusions from the well-investigated analogous stannyl compounds (172) can be transferred. Thus the  $\text{R}_3\text{Pb}$  grouping should be planar and at a right angle to the  $\text{N}-\text{Pb}-\text{N}$  bond.

Little is known about the properties of plumbylamines except for the reactions which are reported below.

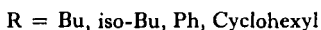
### B. Ligand Exchange, Protolysis

The high reactivity of the Pb—N bond has already been seen in the easy hydrolysis of the dialkylplumbylamines  $R_3Pb-NR'_2$ . Generally the following equation is true:



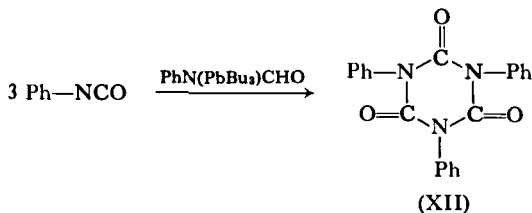
Thereby X, besides OH (as reported above, some plumbylamines are resistant towards hydrolysis) may be *O*-acyl, halogen or another acid group, OR, or the group of a higher boiling amine. The instability of many plumbylamines at elevated temperatures has to be considered during these exchange reactions. These reactions have not yet been systematically examined. In view of the extensive results from the stannylamines (127, 189) and the generally increased reactivity of the Pb—N bond compared to the Sn—N bond, it can be assumed that numerous compounds with an acidic H atom may be substituted into the above equation for HX.

$Ph_3GeH$  undergoes a slightly exothermic reaction with plumbylamines even at 20° C, to give light yellow compounds with Pb—Ge bonds (only the Bu derivative is an oil) (196).  $Et_3GeH$  and  $Ph_3SiH$ , however, are inert.



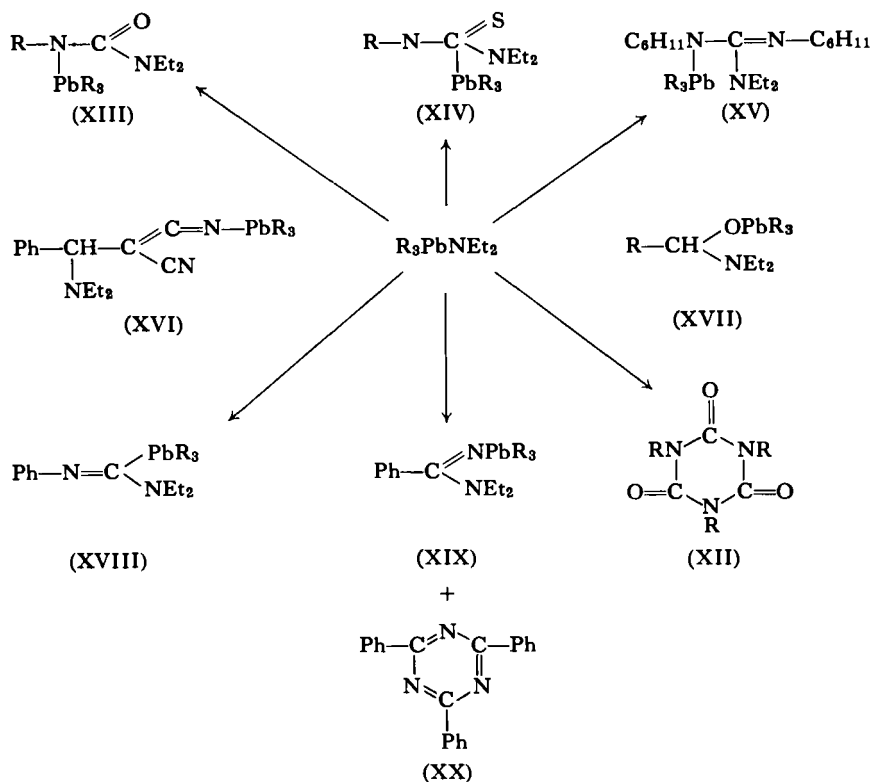
### C. Aminoplumbation of Polar Unsaturated Systems

Aminometallation reactions have been shown to be useful in synthesis (152, 197), not only with Sn—N compounds, but also with amine derivatives of B, Si, P, As, S, Zn, and Hg (127, 205). Because the organolead grouping can generally be cleaved easily, this reaction should be important for the introduction of amino groups. We confirmed this conclusion when we reacted  $Bu_3PbH$  with an excess of phenylisocyanate. The adduct initially formed catalyzes trimerization (188, 194).



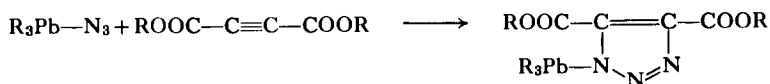
A chain of additions of the Pb—N grouping to the —NCO grouping is assumed. Finally as the ring is formed, the catalytic molecule is separated and can be used again for further cyclization. This view was confirmed by the use of a small amount of  $\text{Bu}_3\text{PbNEt}_2$  as catalyst. With  $\text{R} = \text{Ph}$ , Et, Bu the trimer (XII) is formed spontaneously at  $-50^\circ\text{C}$ ; with  $\text{R} = \text{cyclo-C}_6\text{H}_{11}$  at  $20^\circ\text{C}$  only after 2 days, but practically quantitatively. From di- or triisocyanates one obtains polymers exothermically, which are not soluble in the usual organic solvents.

But the 1:1 adduct (XIII) is easily formed by slowly dropping phenyl isocyanate into equimolar amounts of  $\text{Bu}_3\text{PbNEt}_2$  and petroleum ether. Hydrolysis gives the *N*-phenyl-*N'*-diethylurea. Cyclohexylisocyanate reacts the same way. From ethyl isothiocyanate oil the adduct (XIV) seems to be formed, but the possibility of an addition to the  $\text{C}=\text{S}$  group is not excluded. In any case triethylthiourea is slowly formed with water. Dicyclohexyl carbodiimide reacts to give *N*-plumbylguanidine (XV), in which the



Pb—N bond is easily hydrolyzed. Benzylidenemalonodinitrile forms the adduct (XVI) which reacts only very slowly with ethanol at 60° C (stabilization could be possible by pentacoordination of lead) and is completely hydrolyzed by water only after 24 hours at 60° C. Propionaldehyde, slowly added to plumbylamine, reacts exothermically to form the adduct (XVII), as does *p*-tolualdehyde. After hydrolysis, the aldehyde is mainly recovered, possibly by cleaving HNEt<sub>2</sub> from  $\alpha$ -hydroxyamine. Phenylisocyanide gives the *C*-plumbylamidine (XVIII), which reacts with dry HCl gas to give the lead-free amidine. Two competing reactions are found with benzonitrile; addition gives the amino derivative (XIX), from which by hydrolysis the lead-free amidine is formed. Also the catalytic trimerization of the nitrile to the triazine kyaphenin (XX) takes place. This compound (XX) crystallizes during the reaction (152, 157).

Henry *et al.* (95) found that a normal addition of the azide group to acetylene dicarboxylic acid ester formed the Pb—N bond.



However, some other alkynes, malonic acid anhydride and ester, vinyl ethyl ether, and a substituted cyclopentene do not react. On the other hand the azides of the type Ph<sub>3</sub>Pb(CH<sub>2</sub>)<sub>*n*</sub>N<sub>3</sub> (Table III) give, even with poor dipolarophiles, the expected 1,3-addition (95).

Certainly other preparative uses of the plumbylamines should be investigated in future experiments.

## V

### THE Pb—O BOND

#### A. Preparation and Reactivity of Organolead Oxides, Hydroxides, and Alkoxides

##### 1. Organolead Oxides and Hydroxides

Compounds of this kind were mentioned in the literature long ago. In most cases they are synthesized from the appropriate derivatives R<sub>3</sub>PbX, R<sub>2</sub>PbX<sub>2</sub>, or RPbX<sub>3</sub>, respectively (X = halogen, acylate, nitrate), by the use of alkali, Ag<sub>2</sub>O, or water in aqueous or alcoholic solution (Table XIV).



Today good results can be obtained by hydrolysis of the easily available trialkyl methoxides (44); see Section V,A,2.

Not much is known about the products and it is generally accepted that the hydrolysis of  $R_3PbX$  should give the corresponding hydroxide,  $R_3PbOH$ . Probably the reaction is not as simple. At least in some of the reactions an equilibrium with the hydrated plumbosane has to be postulated.

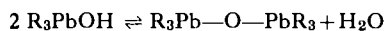


TABLE XIV  
ORGANOLEAD OXIDES AND HYDROXIDES

Compound	Method <sup>a</sup>	Properties	References
$R_3PbOH$ ; R = Me, Et Pr, Bu, cyclo-Hexyl	C, H	Not much characterized after prepared in solution	18, 161
$Ph_3PbOH$	C, H	Crystals, m.p. 300°–310° C colorless	161, 271
$Ph_2(C_6H_4-o-COOH)PbOH$	A	M.p. 300°–305° C	83
$(Et_3Pb)_2O$	H	Decomp. 70°–80° C	4
$(Ph_3Pb)_2O$	F	Solid, colorless	31
$(Ph_2PbOCOR)_2O$ R = Me, <sup>b</sup> Pr, iso-Pr, Ph, 2-Naphthyl	E	Dec. 218°–260° C	217, 282
$Ph_2Pb(OH)OAc$	D	Dec. when melted	217
$R_2Pb(OH)_2$ ; R = Et, Ph, NH <sub>2</sub> Ph	C, G, H	Almost not characterized	139, 246
$R_2PbO$ ; R = Me, Et, Ph, <i>p</i> -MePh, O <sub>2</sub> NPh	C, D, F, G	Almost not characterized	18, 103, 137, 217, 246
" $RPb(OH)_3$ "; R = Me, Et, Pr, iso-Bu, Bu, All, Ph, Benz	B	Amorph, dec. slowly at 35° in air, almost not characterized <sup>c</sup>	163
" $ArPb(O)OH$ "; Ar = Ph, <i>p</i> -MePh, <i>p</i> -MeOPh, 1- and 2-Naphthyl	B, D	Amorph, almost not characterized <sup>c</sup>	137, 170

<sup>a</sup> A, Dealkylation reaction, e.g., with  $KMnO_4$ . B, Alkylation of lead oxide,  $PbO \cdot H_2O + RI \rightarrow RPb(OH)_3$ . C, Reactions of organolead halides with  $Ag_2O$  or alcoholic KOH (NaOH). D, Reactions of organolead nitrates or carboxylates with KOH,  $H_2O$ ,  $NH_4OH$ . E,  $R_2Pb(O_2CR)_2 + CH_2=N_2 \rightarrow (R_2PbO_2CR)_2O$ . F, Interconversion reactions,  $Et_3Pb(OH)_2 \rightarrow Et_3PbO$  (over conc.  $H_2SO_4$ );  $2 R_3PbOH \rightarrow (R_3Pb)_2O$ . G,  $(O_2NC_6H_4)_2PbO + TiCl_3 + HCl \rightarrow (H_2NC_6H_4)_2PbO$ .  $Ph_2Pb(OAc)_2 + HNO_3 \rightarrow (O_2NC_6H_4)_2PbO$ . H, Oxidation of  $R_3Pb_2$ .

<sup>b</sup> Instead of  $Ph_2$  also (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>.

<sup>c</sup> To the problem of the structure compare experiments on the corresponding "alkylstannic acids" (189).

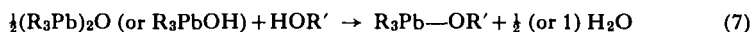
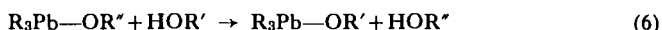
Furthermore the recently established pentacoordination of the lead atom which leads to association (perhaps dimerization) of the molecules has to be considered. What actually happens certainly depends on R and the solvent. Also in the case of the plumboxanes  $R_3Pb-O-PbR_3$  dimerization must be considered, at least in the presence of negative R groups, e.g.,  $AcO-R_2Pb-O-PbR_2-OAc$ .

Little is known about  $R_2Pb(OH)_2$  compounds. Dehydration is possible to give  $R_2PbO$ , which could be a polymer, perhaps cyclic. Even less known are the "alkylplumbonic acids,  $RPb(O)OH$ " and their hydrated form " $RPb(OH)_3$ ." The first certainly does not exist as a monomer.

Because so little is known about the products it only can be assumed that similar relations as for the analogous organotin compounds (189) hold, that is, that the dialkyllead oxides are in fact polyplumboxanes ( $-R_2Pb-O-$ )<sub>n</sub>, perhaps cyclic with  $n=3$  or 4. The "alkylplumbonic acids" could then have similar but cross-linked structures. A number of plumbosiloxanes are known (52, 245), as well as other compounds with  $Pb-O-M$  groupings (52).

## 2. Organolead Alkoxides

Whereas organotin alkoxides are well known and useful for different syntheses (189), little was known until recently about organolead alkoxides (52, 161, 273). Some compounds were mentioned before 1965 (4, 84) but since then Amberger and Hönigschmidt-Grossich (10) and Davies and Puddephatt (42, 44) have reported systematic investigations. Three methods are useful for the synthesis of trialkyllead alkoxides.



For the methoxides Eq. (5) is favored (10, 42, 44); for the alkoxides with larger  $R'$  groups, the alcoholysis of methoxides according to Eq. (6) is to be favored. Methanol together with the added excess of  $R'OH$  is distilled. Condensation according to Eq. (7) may also be used, removing water as it is formed azeotropically with benzene or toluene (44). Table XV shows the compounds of the type  $R_3PbOR'$  prepared up to now.

The reaction of  $(R_3Pb)_2O$  or  $R_3PbOH$  with dialkyl carbonates to prepare the alkoxides shows no advantages and often leads to mixtures (44).

The compounds  $R_3PbOR'$  are liquids or crystalline compounds which usually can be purified by distillation or sublimation under vacuum, but decompose easily if stored for several days at 20° C even in a sealed tube (except if  $R=Ph$ ). From  $Et_3Pb-OMe$ ,  $Et_4Pb$  is mainly formed. The alkoxides are soluble in most of the usual organic solvents; they are monomeric (44) but are easily decomposed even by humid air. They can be analyzed by titration with acid (because of the basicity of the hydroxides set free during the hydrolysis). Detailed IR and NMR studies have been made (44). Further details can be seen in Table XV.

Organolead peroxides, mainly of the type  $R_3Pb-OOR'$ , are relatively well known (4, 236, 256). The same is true for the various types of plumbyl esters of carboxylic acids (52).

The  $Pb-O$  bond is far more reactive than the  $Sn-O$  bond (189), but is similar to the  $Sn-N$  bond. Because the plumbyl group is generally easily cleaved during a second step, a specific preparative use is provided.

TABLE XV  
ORGANOLEAD ALKOXIDES

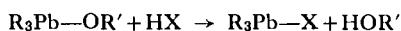
Compounds	Method <sup>a</sup>	Properties (°C/mm)	$\nu_{C-O}$ ( $cm^{-1}$ )	References
$Me_3PbOMe$	A	Dec. at 250°; subl. 70°–100°/0.05	1042	10, 44
$Me_3PbOEt$	B	M.p. 113°–115°; subl. 60°–80°/0.1	1044	44
$Me_3PbOPr$	B	M.p. 128°–131°; subl. 70°–100°/0.3	1054	44
$Me_3PbO-iso-Pr$	C	Solid	—	44
$Me_3PbO-tert-Bu$	C	Solid	—	44
$Me_3PbO-neopentyl$	C	Liquid	—	44
$Et_3PbOMe$	A	M.p. 81°–83°; subl. 50°–80°/0.05	1042	10, 44
$Et_3PbOEt$	B	M.p. 37°–39°; b.p. 51°–53°/0.04	1050	4, 44
$Et_3PbOPr$	B	B.p. 74°–76°/0.2	1064	44
$Et_3PbO-iso-Pr$	B	B.p. 48°–50°/0.05	1121	44
$Et_3PbOBu$	B	B.p. 78°–79°/0.05	1072	44
$Et_3PbO-iso-Bu$	B	B.p. 56°–58°/0.1	1062	44
$Et_3PbO-tert-Bu$	B	B.p. 58°–60°/0.2	1191	44
$Et_3PbO-neopentyl$	B	B.p. 107°–110°/0.1	1071	44
$Et_3PbO-cyclohexyl$	C	B.p. ~ 110°/0.1	—	44
$Et_3PbOCH_2Ph$	C	No information		4
$Et_3PbOCHMePh$	C	B.p. ~ 110°/0.05	1153	44
$Et_3PbOCMe_2Ph$	C	Yellowish-green oil		4
$Bu_3PbOMe$	A	M.p. 46°–48°, subl. 70°–100°/0.02	1040	10, 44
$Ph_3PbOMe$	A	M.p. 90°–91°	1035	44

<sup>a</sup> Methods: A, Eq. (5); B, Eq. (6); C, Eq. (7).

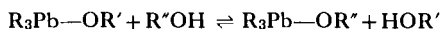
In the following reactions, the alkoxides  $R_3Pb-OR'$  are generally mentioned as examples. But in most cases the hydroxides,  $R_3PbOH$ , plumboxanes,  $(R_3Pb)_2O$ , and also plumbyl esters, i.e.,  $R_3PbOCOR'$  should react similarly.

### B. Ligand Exchange, Protolysis

Like the  $Pb-N$  bond (see Section IV,B) the  $Pb-O$  bond is also easily affected by exchange reactions. Hydrogenation to  $Pb-H$  with  $B_2H_6$  (11) was already mentioned in Section III,A,1,b. Proton-donating substances, including iron carbonyl hydrides (104), react at once (42, 44).



X may be OH, but *O*-acyl, and halogen or another acid group are better. With other alcohols the ligands are exchanged. The equilibrium can be shifted quantitatively to the right if  $R'OH$  is lower boiling than  $R''OH$  and is distilled off.

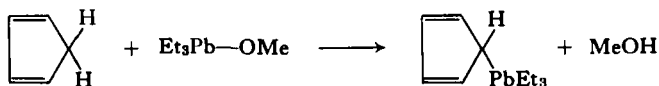


This renders the preparation of other alkoxides, e.g., methoxides, very easy; see Section V,A,2.

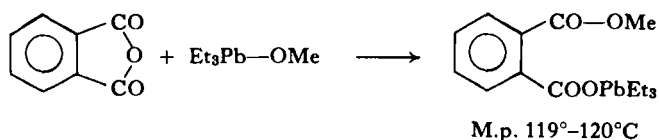
Even haloforms react according to the HX outline at  $20^\circ C$  ( $R=Ph$  or  $Et$ ,  $X=Cl, Br$ ) (44).



The trihalomethyllead compounds, e.g.,  $Ph_3Pb-CCl_3$  (m.p.  $171^\circ-171.5^\circ C$ ) or  $Ph_3Pb-CBr_3$  (m.p.  $135^\circ-140^\circ C$ ), can be prepared differently too, see Section II,C; the former have also been prepared from  $CCl_4$  and  $Ph_3PbLi$  (274). Other CH acidic compounds condense, e.g., cyclopentadiene (44).



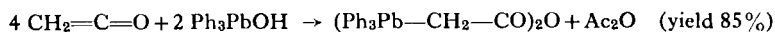
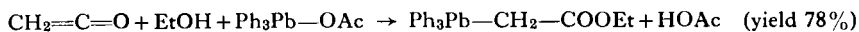
For the mechanism, a nucleophilic attack of the alkoxy oxygen on H and, in the same way, of X on the plumbyl group must be considered. Since one can generally substitute  $A-B$  for  $HX$ , it comes out that the possibilities of this type of reaction are not limited by the given examples. Rather, all the parts of the reactants can remain in the product, e.g., in the case of phthalic acid anhydride.



The products thus formed are useful for the characterization of the compounds  $R_3Pb-OR'$ .

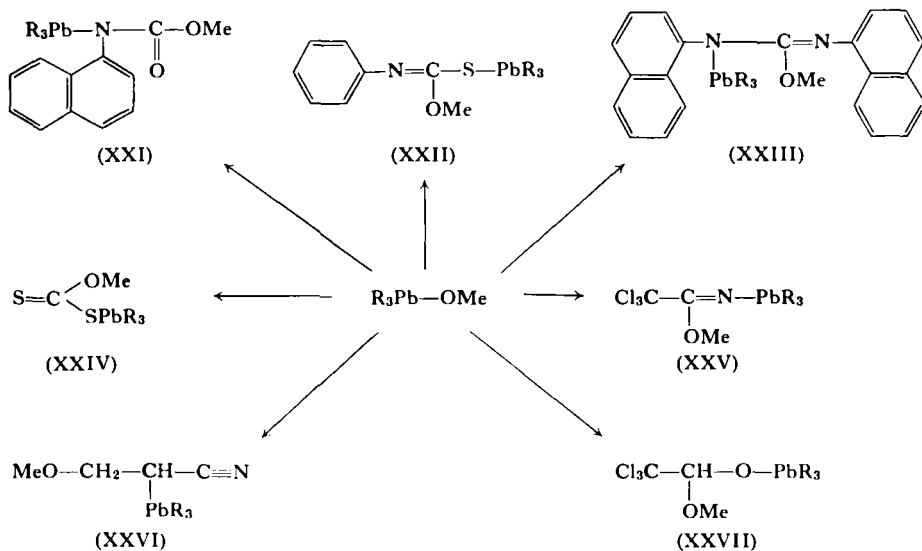
### C. Oxyplumbation of Polar Unsaturated Systems

The first known examples were the addition of a plumbyl ester or hydroxide to ketene (276).



Corresponding to the known properties of ketene, only the  $C=C$  group reacts and the plumbyl grouping is bound to carbon. In most of the other additions (see below) the plumbyl grouping is bound to the hetero atom.

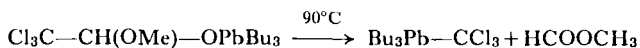
The following reactions of the  $Pb-O$  bond have to be seen in appropriate relation to the  $Pb-N$  bond (see Section IV,B) and the reactions of the  $Sn-O$  and  $Sn-N$  bonds (189). The reactivities decrease in the following manner:  $R_3Pb-NR_2 > R_3Pb-OR' > R_3Sn-NR_2' > Ar_3Pb-OR' > R_3Sn-OR'$ .



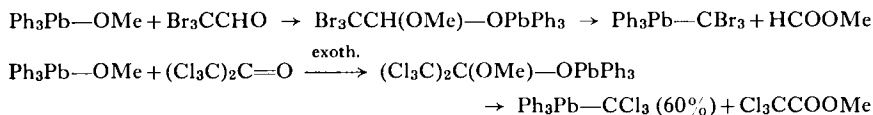
The high reactivity of the Pb—O bond raises the question whether oxyplumbation is of importance in the often useful reactions of lead tetraacetate (40), as is commonly assumed. At least, oxyplumbation is postulated for the cleavage of the cyclopropane ring by Pb(OAc)<sub>4</sub> (212) as in the reaction of styrene with acetylacetone in the presence of Pb(OAc)<sub>4</sub> (119).

A whole series of additions to polar unsaturated bonds, seemingly following a polar mechanism, was recently reported by Davies and Puddephatt (42, 44).

1-Naphthyl isocyanate reacts exothermically with R<sub>3</sub>Pb—OMe (R = Bu or Ph) to give an *N*-plumbylcarbamine acid ester (XXI), which is easily hydrolyzed to 1-C<sub>10</sub>H<sub>7</sub>NHCOOMe. Therefore in the case of (XXI), addition to the N=C bond has to be proposed, but addition to C=O has not yet been excluded. Ph<sub>3</sub>PbOMe and Bu<sub>3</sub>PbOMe also catalyze trimerization of the isocyanate, as they catalyze the addition of methanol to BuNCO and bis(1-naphthyl) carbodiimide. Phenylisothiocyanate reacts exothermically with Ph<sub>3</sub>Pb—OMe to give the adduct (XXII) which is stable in air; the corresponding Bu<sub>3</sub>Pb derivative decomposes. Bis(1-naphthyl) carbodiimide reacts quickly to give the isomer (XXIII) (monomeric in benzene). With CS<sub>2</sub> a stable dithiocarbonate (XXIV) (R = Ph) is formed; the corresponding product with R = Bu decomposes. Also the nitrile group adds to the Pb—O bond; from trichloroacetonitrile the imide derivative (XXV) is exothermically formed. It is easily hydrolyzed to Cl<sub>3</sub>C—C(OMe)=NH. Acrylonitrile also reacts exothermically with addition to the C=C group. The adduct formed has, according to spectroscopic data, the structure (XXVI). Thus there is a polar mechanism also in this case, where Pb—O addition is oriented by polarization of the C=C group. This addition is clearly reversible. There is no 1,4-addition, as in the case of organolead hydrides (see Section III, B, 3). Trichloroacetaldehyde gives the adduct (XXVII), which if melted yields Ph<sub>3</sub>PbCl in the case where R = Ph, but with R = Bu formic acid ester and Bu<sub>3</sub>PbCCl<sub>3</sub> seem to be formed.



This reaction leads to a new way for preparing trialkyl trihalogenomethyl lead compounds (compare the reaction with HCX<sub>3</sub>; see Section V, B). These reactions work also with tribromoacetaldehyde and with hexachloroacetone (42, 44).



The products mentioned in Section V,C are mostly isolated in a pure form and identified not only by analysis and melting points, but also by IR and NMR spectroscopic investigations and often by isolating the products of hydrolysis. Molecular weight determinations show that the plumbyl compounds (XXI)–(XXVII) are monomeric in solution (42, 44).

There are many other possibilities for synthesis with the Pb—O bond and further research on this topic will be of great value.

### Final Note

From recent developments it can be expected that in the future organic lead compounds will be examined in more laboratories than is the case now or in the past. Therefore, we want to remind chemists of the possible danger in working with these compounds (review of the literature, see Dub, 52). Contact of lead alkyls with the skin and inhalation of their vapors must be avoided. Efficient hoods, rubber gloves, and careful experimentation are presupposed. Also cleaning of the apparatus and the removal of the waste products should be done with care.

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## ***Cumulative List of Contributors***

- Abel, E. W., 5, 2  
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Armitage, D. A., 5, 2  
Atwell, W. H., 4, 1  
Bennett, M. A., 4, 353  
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